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CO_2 migration and reaction in cementitious repositories: A summary of work conducted as part of the FORGE project.

Minerals and Waste Programme

Open Report OR/13/004

BRITISH GEOLOGICAL SURVEY

MINERALS AND WASTE PROGRAMME

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C.A. Rochelle, G. Purser, A.E. Milodowski, D.J. Noy, D. Wagner, A. Butcher and J.F. Harrington

Keywords

Report; radioactive waste, cement, backfill, CO_2, gas, carbonation.

Front cover

High-resolution map of calcium abundance within partly-carbonated Nirex reference backfill cement. Pink and yellow colours represent high calcium abundance. The leading edge of a carbonation front runs through the centre of the image. The front was moving from right to left.

Bibliographical reference

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Euratom 7th Framework Programme Project: FORGE

EURATOM

Fate of repository gases (FORGE)

The multiple barrier concept is the cornerstone of all proposed schemes for underground disposal of radioactive wastes. The concept invokes a series of barriers, both engineered and natural, between the waste and the surface. Achieving this concept is the primary objective of all disposal programmes, from site appraisal and characterisation to repository design and construction. However, the performance of the repository as a whole (waste, buffer, engineering disturbed zone, host rock), and in particular its gas transport properties, are still poorly understood. Issues still to be adequately examined that relate to understanding basic processes include: dilational versus visco-capillary flow mechanisms; long-term integrity of seals, in particular gas flow along contacts; role of the excavation damaged zone (EDZ) as a conduit for preferential flow; and laboratory to field up-scaling. Understanding gas generation and migration is thus vital in the quantitative assessment of repositories and is the focus of the research in this integrated, multi-disciplinary project. The FORGE project is a pan-European project with links to international radioactive waste management organisations, regulators and academia, specifically designed to tackle the key research issues associated with the generation and movement of repository gases. Of particular importance are the long-term performance of bentonite buffers, plastic clays, indurated mudrocks and crystalline formations. Further experimental data are required to reduce uncertainty relating to the quantitative treatment of gas in performance assessment. FORGE will address these issues through a series of laboratory and field-scale experiments, including the development of new methods for up-scaling allowing the optimisation of concepts through detailed scenario analysis. The FORGE partners are committed to training and CPD through a broad portfolio of training opportunities and initiatives which form a significant part of the project.

Further details on the FORGE project and its outcomes can be accessed at www.FORGEproject.org.

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Contents

FIGURES

TABLES

Summary

Some repository concepts envisage the use of large quantities of cementitious materials – both for repository construction and as a buffer/backfill. However, some wastes placed within a subsurface repository will contain a significant amount of organic material which may degrade to produce carbon dioxide (CO_2). This will react with cement buffer/backfill to produce carbonate minerals such as calcite, which will reduce the ability of the buffer/backfill to maintain highly alkaline conditions and as a consequence its ability to limit radionuclide migration. The reaction may also alter the physical properties of the buffer/backfill.

The work presented here summarises the findings of a study conducted within the laboratories of the British Geological Survey into the impact of CO_2 on a relatively permeable potential repository cement (Nirex reference vault backfill, NRVB). The work investigated reaction-transport processes through elevated pressure laboratory experiments conducted at a range of likely future *in-situ* repository conditions. These provide information on the reactions that occur, with results serving as examples with which to test predictive modelling codes.

Thirty-two static batch experiments were pressurised with either CO_2, or with N_2 for 'non-reacting' comparison tests. Twenty six of these were left to react for durations of between 10-40 days, with six more left to react for a year. The aim of them was to help investigate mineralogical and fluid chemical changes due to the diffusional ingress of CO_2 into unconfined NRVB samples measuring 2.5 cm in diameter and 5 cm long. Four flow experiments were also conducted, aimed at quantifying changes in the transport properties of the buffer/backfill cement under likely *in-situ* conditions as a consequence of carbonation due to the advection of free phase or dissolved CO_2.

All the cement samples showed rapid reaction with CO_2, manifested by a colour change from grey to light brown. The cement blocks remained intact, even after prolonged exposure to CO_2-rich fluids. Carbonation was associated with an increase in weight by up to 9%, though the samples did not change in overall size. Free phase CO_2 gave slightly more reaction than dissolved CO_2, possibly because of its higher concentration and greater ability to penetrate the samples. In terms of major reactions during carbonation, these were the breakdown of portlandite and calcium silicate hydrate (CSH) phases and the formation of carbonate phases and silica gel. The observed colour change was possibly caused by CO_2-enhanced reaction of small amounts of calcium ferrite minerals in the cement and liberation of the ferric iron to give a 'rusty' colour.

Carbonation resulted in a series of reaction fronts that moved through the cement over time. These fronts separated several reaction zones: Zone 1 = minor carbonation with minimal apparent volume change, Zone 2 = partial carbonation and very localised shrinkage, Zone 3 = complete conversion of portlandite and CSH with localised shrinkage associated with the development of calcium carbonate-sealed microfractures, Zone 4 = dissolution of initially-formed carbonate minerals in the outermost parts of the sample by the surrounding, slightly-acidic water. The shrinkage in Zone 2 was expressed as small fractures (typically several mm long), though these do not appear to extend beyond this zone. Zone 3 contained an anastomising '3D chickenwire' meshwork of interconnected, higher-density, carbonate-filled microfractures (typically on a 10s-100s μm scale) that separated silica-rich areas having lower-density and high porosity, and sub-parallel 'relic' reaction fronts. The small fractures of Zone 2 appear to have filled with secondary precipitates in Zone 3. Appreciable amounts of a Cl-rich phase were formed at the boundary of Zones 2 and 3, which was aided by the presence of CO_2. The formation of Cl-rich phases within a repository could be beneficial as it might help to immobilise ^{36}Cl leaching from the waste.

Controlled flow-rate carbonation experiments on 5 cm diameter by 5 cm long cores of NRVB cement reveal decreases in overall sample permeability. These reflect porosity reduction due to conversion of portlandite and CSH to secondary carbonate minerals and silica gel. Small

discharges of water were also released as a by-product of CSH phase carbonation. Detailed petrographic observations of partly-reacted cement samples show a series of reaction zones as per the static experiments. These observations, coupled with micropermeameter data, show the greatest reductions in porosity and permeability in a very narrow zone at the leading edge of the visible alteration front. Injection of free-phase (gaseous and supercritical) CO_2 resulted in a halving of permeability, whereas use of dissolved CO_2 reduced hydraulic permeability by about 3 orders of magnitude. These reductions could be beneficial within a repository setting, as they reduce the potential for radionuclide migration. Carbonation did not lead to complete blockage of the cement however. CO_2 migration was still possible (though to a reduced extent), so in a repository setting there is still potential for the cement to vent gas with a view to preventing build-up of pressure in and around the waste canisters.

Carbonation features and secondary phases observed in these experiments using a relatively porous/permeable cement, bear many similarities to those found in far lower porosity/permeability borehole cements used in CO_2-storage operations. There are also similarities to samples of naturally-occurring CSH phases which have been naturally-carbonated over prolonged timescales. A number of common carbonation processes may be operating in all these systems.

1 Introduction

Some repository concepts envisage the use of large quantities of cementitious materials – both for repository construction and as a buffer/backfill. Key aspects of these materials are their good mechanical properties and their ability to buffer pH to alkaline conditions. Such high pH conditions are important as they greatly limit metallic corrosion and radionuclide solubility - and as a consequence, radionuclide migration. Some wastes placed within a subsurface repository will contain a significant amount of organic material (e.g. ion-exchange resins, contaminated clothing etc). Over time, these may degrade to produce carbon dioxide (CO_2), which will react rapidly with cement buffer/backfill to produce carbonate minerals such as calcite. This may be beneficial in terms of immobilisation of ^{14}C as a carbonate if it were present. Carbonation reactions occurring on the *inside* of the repository cement will be quite separate to those occurring on the *outside* of the repository cement (through interaction with surrounding carbonate groundwaters), though they may share very similar reaction mechanisms.

The conversion of cement minerals to carbonates will reduce the ability of the buffer/backfill to maintain highly alkaline conditions and as a consequence its ability to limit the migration of certain radionuclides. However, the reaction may also alter the physical properties of the buffer/backfill, possibly changing its permeability and strength. Although carbonation reactions might improve some properties, it is currently unclear whether the *overall* changes due to carbonation will be beneficial to long-term radionuclide immobilisation, or deleterious.

This study investigated the effects of cement carbonation processes via laboratory experiments conducted at a range of likely future *in-situ* repository conditions, including those expected over glacial timescales, which might influence the form of the carbon dioxide. Thus the experiments were run under conditions representative of those that might be found currently within a deep repository or potentially in the future, with temperatures between 20-40 °C and pressures between 40-80 bar (equivalent hydrostatic heads of approximately 400-800 m) (Figure 1). Within this range of conditions, the phase behaviour of CO_2 is such that it can exist in gaseous, liquid, or supercritical states, as well as dissolved in water in contact with these states. The results of the experiments will serve as examples with which to test predictive modelling codes that incorporate reaction kinetics, and coupling between geochemical reaction, porosity changes and fluid flow.

Two types of experiments were conducted within the BGS Fluid Processes Laboratories:

1) Numerous batch experiments to provide information on changing mineralogy and porosity upon reaction with free phase and dissolved gaseous, liquid and supercritical CO_2. A detailed description of these experiments is given in Rochelle and Purser (2010), Rochelle et al. (2014) and Milodowski et al. (2013). These experiments involved samples that were unconfined, with reactions controlled by diffusion of free-phase or dissolved CO_2 into the cement. Three cement pore fluids were utilised with compositions based on previous calculations of those anticipated in the vicinity of a cementitious waste repository (Bond et al., 1995a,b):

    - A young pore fluid of high pH and with a significant component of NaOH and KOH (‘young near field porewater’ - YNFP).
    - A slightly lower pH pore fluid with a significant proportion of Na, K and Cl, and some Ca and OH (‘YNFP + Cl’).
    - An evolved pore fluid representing equilibration of groundwater with cement, and having lower pH and a chemistry dominated by $Ca(OH)_2$ (‘evolved near field groundwater’- YNFG).

2) Four flow experiments with gaseous, supercritical and dissolved CO_2 were undertaken, and were aimed at providing information on changing permeability upon reaction. A detailed description of these experiments, and the results from them, is given in Purser et al. (2013a,b). These experiments involved samples confined within Teflon™ jackets, and held within a uniform confining pressure. Free–phase or dissolved CO_2 was pumped through the samples, with input/output flow rates and pressures used to derive permeability data.

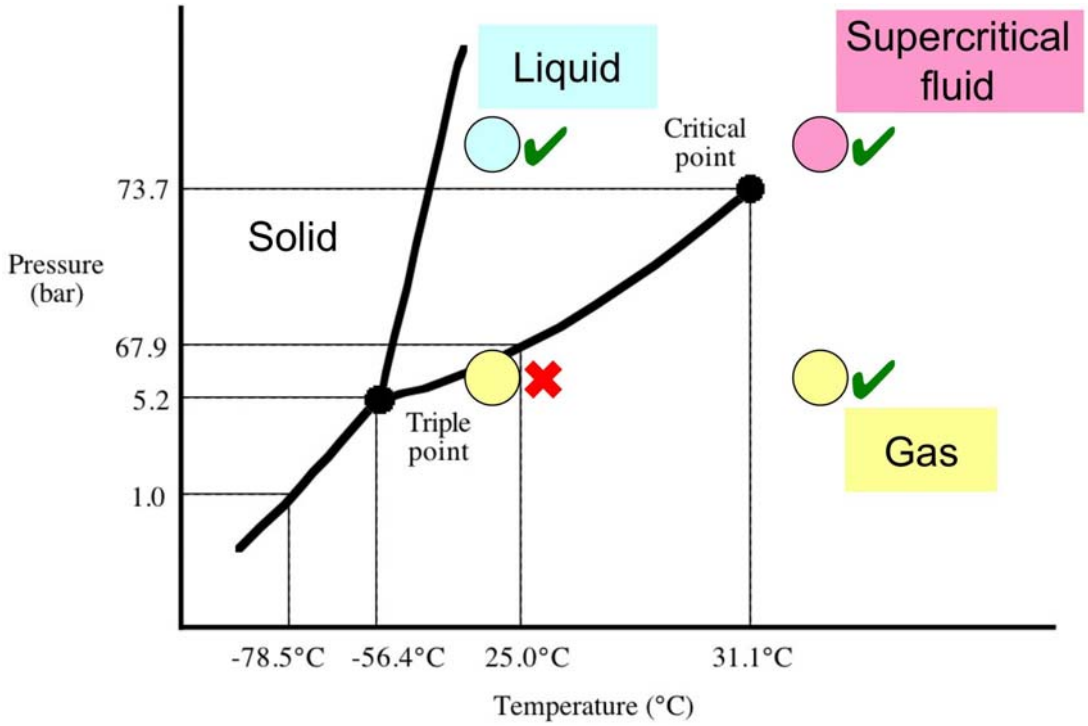


Figure 1 Experimental run conditions plotted on a phase diagram for CO_2. Conditions were 20° and 40°C, and 40 and 80 bar, though only 3 of the possible 4 combinations of these were studied.

Within a repository setting buffer/backfill cement has at least two key notable functions; to maintain highly alkaline conditions and hence reduce radionuclide solubility, and to allow controlled escape of gas away from waste canisters. As a consequence of the need for the latter of these functions, the cement is relatively permeable compared to some other cements (e.g. such as those used for borehole sealing). Some gases generated within the repository (such as hydrogen) may undergo very limited chemical reactions once formed, and hence their migration will be largely controlled by transport processes. CO_2 on the other hand, is highly reactive towards cement minerals, and so its migration will be controlled by a complex interplay between transport processes and chemical reactions.

The cement composition used was the Nirex reference vault backfill (NRVB) cement (Francis et al., 1997). It consisted of approximately: 26% Portland cement, 28.6% limestone powder, 9.8% lime, and 35.6% water. The mixture was cast into cylindrical blocks of approximate size 12 cm diameter by 30 cm long, and was cured for at least 40 days prior to subsampling for use in the experiments - see Rochelle and Purser (2010) for more details. Use of this cement allows the present study to be comparable with measured parameters/datasets from earlier studies. It is acknowledged however, that the compositions of backfill cements used in any future repository may well be different to that used in this study, but it is considered that many of the reaction processes we observed are likely to be common to a wide-range of cements.

2 Summary of experimental results

2.1 STATIC BATCH EXPERIMENTS

A detailed description of these experiments is given in Rochelle and Purser (2010) and Rochelle et al., (2014), and only a summary is presented here. The aim of these experiments was to investigate fluid chemical, mineralogical, and textural changes upon diffusion-controlled CO_2-cement reaction. The batch equipment used consisted of 316 stainless steel pressure vessels with wetted parts lined with PTFE (polytetrafluoroethene) 'cups', high pressure tubing was made of either 316 stainless steel or titanium, and O-ring seals were made of Viton®. The large blocks of cured NRVB were sub-cored to produce samples of 25 mm diameter and of 50 mm long, and one of these cores was placed into each vessel, usually by attaching it to the fluid sample tube (Figure 2). This tube remained in place whether or not the experiment contained an aqueous phase or just free-phase CO_2. Several experiments were run at the same time, and were often connected to the same pressure line to maintain uniform conditions between them (Figure 3). Temperature control was achieved through the use of either a LMS thermostatically-controlled incubator for experiments at 20 °C, or a Gallenkamp Plus2 oven for experiments at 40 °C (both accurate to better than ± 0.5 °C).

Where used, a quantity (approximately 230 g) of cement porewater was placed into the PTFE liner of the vessel, together with a small magnetic stirrer bead to ensure good mixing of the fluids. The total volume of the solid and aqueous samples filled about 70% of each vessel. For experiments involving both porewater and cement, the fluid:solid mass ratio was about 6:1. No porewater was added to the experiments reacting cement with dry gases. Migration of either free-phase or dissolved CO_2 into the cement was by diffusional processes.

The CO_2 and N_2 were supplied to the reactors from ISCO 500D syringe pumps running in 'constant pressure' mode. The computerised controller allowed the pressure to be maintained to within 0.1 bar (0.01 MPa). Pressure connections were placed at the top of the vessels so that aqueous fluids (denser than high-pressure N_2 or CO_2) could not move out of, or between, the vessels. Vessels pressurised with CO_2 represented the 'reactive cases' and those pressurised with N_2 the 'non-reactive cases'. This allows discrimination between reactions purely due to CO_2, and artefacts that might possibly be introduced by the nature/arrangement of the experiments.

Sampling of the aqueous phase at the end of the experiments was carried out via the titanium dip tube (with a 20 µm pore size polypropylene filter fitted to a PEEK™ (polyetheretherketone) mount at the end), which ran to the base of the PTFE liner. Fluid samples were extracted whilst it was still under run conditions, pressure being maintained through the injection of extra CO_2 into the headspace of the vessel. As much of the aqueous phase as possible was removed during this process to minimise precipitation of misleading carbonate minerals on depressurisation. The reacted cement sample was extracted after the vessel had been carefully depressurised.

On opening the pressure vessels most samples were found to be intact, with the very few breakages possibly being a consequence of over-rapid depressurisation. It was also immediately apparent that the cement had changed appearance in the presence of CO_2, having gone from a mid-grey to a light brown (Figure 4). Cement in contact with N_2 showed little or no colour change. This colour change involving CO_2 is thought to be due to reaction of calcium ferrite minerals and liberation of the iron oxide/oxyhydroxide to give a 'rusty' colour. A similar colour change has been noted for borehole cements exposed to CO_2 (Carrey et al., 2007).

Prior to the start of the experiments accurate measurements were made of the diameter and length of each cement sample. This process was repeated at the end of the experiments, after the core samples had any surface moisture carefully removed, in order to ascertain if reaction with CO_2 had caused any swelling or shrinkage of the cement. No changes in overall sample size were found.

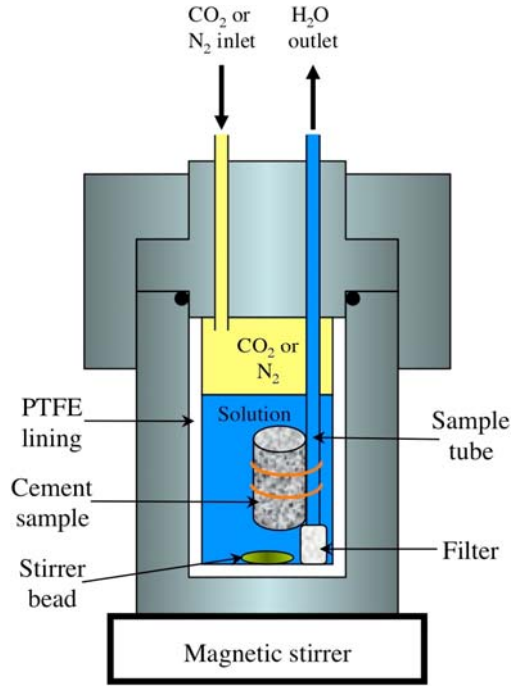


Figure 2 Schematic diagram of an assembled batch reactor.

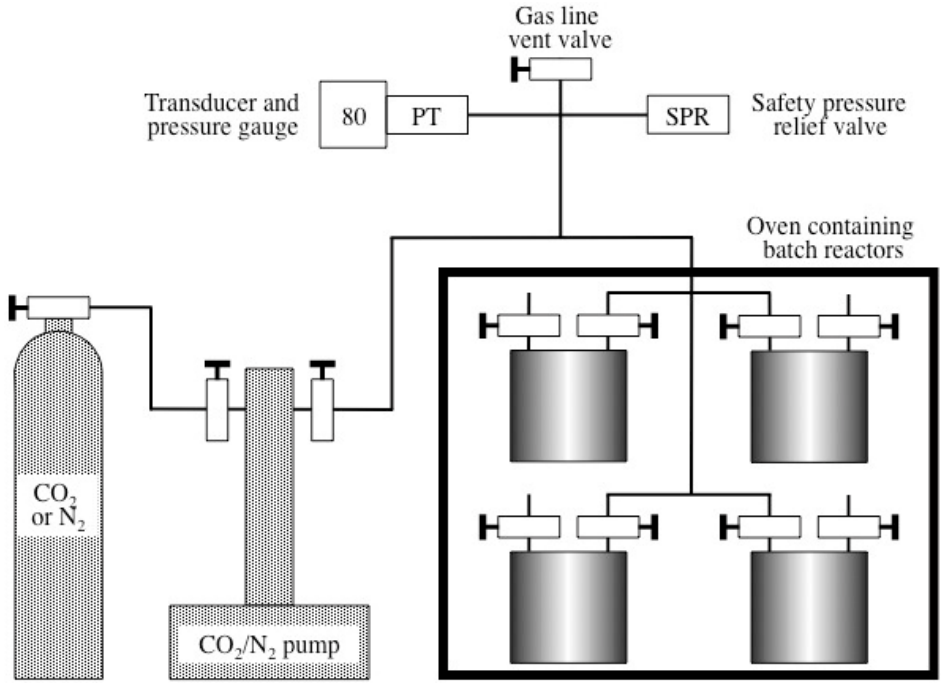


Figure 3 Schematic diagram of the typical layout of batch reactors inside an oven.

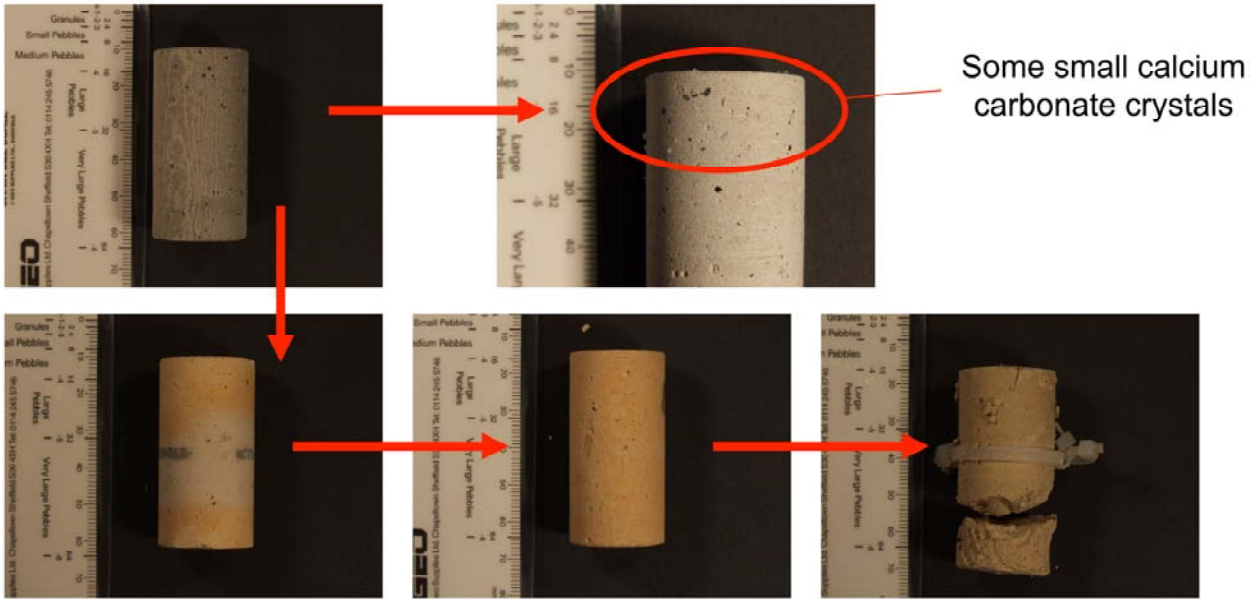


Figure 4 Examples of cement cores before reaction (upper left hand image) and after reaction. Note the grey to brown colour change upon exposure to CO_2, and the appearance of small calcium carbonate crystals on the surface of the cement.

CO_2			Temperature °C							
			20°C				40°C			
			YNFP	YNFP+Cl	ENFG	DRY	YNFP	YNFP+Cl	ENFG	DRY
Pressure (bar)	40 Bar		Gaseous CO_2				Gaseous CO_2			
		40 Days	-	-	-	-	+4.84%	+2.56 %	+2.58 %	+8.20 %
		1 Year	-	-	-	-	-	-	-	-
	80 Bar		Liquid CO_2				Supercritical CO_2			
		10 Days	-	-	-	-	+3.06%		-	-
		20 Days	-	-	-	-	+4.49%		-	-
		40 Days	+4.23%	+5.25 %	+3.57 %	N/A	+5.59%	+7.68 %	+4.50 %	+7.63 %
		1 Year	-	-	-	-	-	+6.84 %	+4.79 %	+8.43 %
							Run 1351: N/A			

N_2			Temperature °C							
			20°C				40°C			
			YNFP	YNFP+Cl	ENFG	DRY	YNFP	YNFP+Cl	ENFG	DRY
Pressure (bar)	40 Bar		Gaseous N_2				Gaseous N_2			
		40 Days	-	-	-	-	+0.69%	-0.75 %	+0.58 %	-2.39 %
		1 Year	-	-	-	-	-	-	-	-
	80 Bar		Gaseous N_2				Gaseous N_2			
		40 Days	+0.65%	+0.97 %	+2.06 %	-3.03 %	+0.30%	+0.12 %	-0.04 %	-3.91 %
		1 Year	-	-	-	-	-	+3.37 %	+2.21 %	-8.83 %
							Run 1350: N/A			

Table 1 Percentage weight changes of cement samples relative to their initial weights after reacting for 10, 20, 40 and 365 days. YNFP is a 'young near-field porewater' dominated by Na-K-Ca, YNFP+Cl was a Na-K-Ca-Cl porewater of more intermediate composition, and ENFG is an 'evolved near-field groundwater' dominated by Ca and containing some Cl.

Cement weight changes

Each sample of reacted cement was carefully weighed at the end of each test and compared with their initial weights (Table 1). Several observations were made:

1) For tests with dry N_2 gas (non-carbonation experiments), all the cement samples lost weight. This seems to have been more pronounced with increasing pressure, temperature and especially timescale. The changes appear to be related to simple dehydration of the cement samples in the dry N_2 gas.

2) For tests with alkaline waters pressurised with N_2 gas (non-carbonation experiments), there is more variation in sample weights. Generally speaking, most samples remained roughly the same weight (within ±1%). There are 3 exceptions to this:

   - The sample reacted at 20°C and 80 bar for 40 days (+2.06%). This weight increase is not typical of similar samples, and was unexpected. It is possible that it may be a consequence of a slightly under-saturated sample at the start of the test, and which took up a little extra water when it saturated during the 40 days of the test.
   - The two samples reacted for a year at 80 bar (+3.37% and +2.21%). These weight increases are thought to represent slow and continuous hydration of previously unreacted cement 'clinker' phases present within the cement during the extended duration of these longer tests.

3) All the tests involving CO_2 (i.e. carbonation experiments) gave cement weight increases (except for the one test where the sample broke up), and these were over and above the weight changes observed in the N_2-pressurised experiments. This is interpreted as carbonation of the cement minerals such as portlandite and CSH gels, with the weight gain being associated with incorporation of the CO_2 into secondary phases.

4) Reaction with CO_2 resulted in weight increases that were more pronounced with increasing timescale, and especially increasing pressure and temperature. The latter two parameters probably increasing the degree of reaction through more CO_2 being present in the reactors, and increased reaction kinetics.

5) The largest weight increases were found in tests with just dry CO_2 (weight increases of approximately 8%). In terms of molar quantities, the carbonation reaction produces at least as much water as amounts of CO_2 consumed (equations [1] and [2]). A dry CO_2 atmosphere would have helped remove this water from the cement sample, facilitating access of more CO_2 to continue the reaction (see Reardon et al., 1989).

6) There are broadly similar weight gains for samples reacted with dry supercritical CO_2 for 40 days and for 1 year. This suggests that the vast majority of the cement carbonation was completed in the first few weeks of reaction.

7) Given that the cement samples did not change size appreciably during carbonation, but did change weight, then their *average* density must have increased.

Mineralogical changes

Most cement samples showed broadly similar changes in mineralogy on carbonation. That said, macroscopic differences appear to be at least partially related to the state of the CO_2 in the experiment. For example, free phase CO_2 gave more pervasive alteration than dissolved CO_2, which is possibly linked to ease of transport into the sample (e.g. Reardon et al., 1989). All cement cores, including those from the N_2 control experiments, showed some minor carbonation on the outside of them (typically 50-100 µm thick), including cores not deliberately exposed to high pressure CO_2. These minor carbonation skins are most likely an artefact of sample handling (e.g. during cutting and exposure to air). They would have formed very rapidly, and prior to the

experiments. This $CaCO_3$ coating is very thin compared to the much thicker experimentally-induced carbonation rinds.

Most cement samples displayed evidence for four main zones:

- Zone 1: A core zone having only very minor carbonation.
- Zone 2: An intermediate zone of partial carbonation.
- Zone 3: An outer zone of complete carbonation.
- Zone 4: The outermost parts of the sample showing dissolution of initially-formed carbonate minerals.

In terms of general reactivity, all 3 phases of CO_2 showed very similar reaction mechanisms with the cement. Key reactions were the conversion of $Ca(OH)_2$ (portlandite) to a secondary carbonate such as calcite, the conversion of CSH phases such as tobermorite to a secondary carbonate and silica gel, and the conversion of calcium ferrites and calcium aluminates to calcium carbonate and iron oxides/hydroxides and aluminium oxides.

$$\underset{\text{portlandite}}{Ca(OH)_2} + CO_2 \Rightarrow \underset{\text{calcite}}{CaCO_3} + H_2O \quad [1]$$

$$\underset{\text{tobermorite (a CSH gel)}}{Ca_5Si_6O_{16}(OH)_2.9.5H_2O} + 5\,CO_2 \Rightarrow \underset{\text{calcite}}{5\,CaCO_3} + \underset{\text{silica gel}}{6\,SiO_2} + 10.5\,H_2O \quad [2]$$

$$\underset{\text{calcium ferrite}}{(CaO)_2.Fe_2O_3} + 2\,CO_2 \Rightarrow \underset{\text{iron oxide}}{Fe_2O_3} + \underset{\text{calcite}}{5\,CaCO_3} \quad [3]$$

All experiments showed evidence for reaction fronts, and right at the leading edge of these there was commonly a very high porosity zone developed (due to dissolution). All experiments also showed a characteristic outer carbonated zone having an anastomising '3D chickenwire' meshwork of interconnected microfractures (typically on a 10s-100s μm scale). Petrography shows these microfractures were initiated at the reaction front as shrinkage cracks, but were subsequently extensively infilled by secondary calcium carbonate. However, predictive modelling (Purser et al., 2013; see Section 2.3) indicates that the complex interplay between mineral reactions, reaction rates, and back diffusion of calcium ions may theoretically result in repeating narrow fronts of $CaCO_3$ precipitation without microfracturing. In some samples, larger shrinkage cracks up to several mm long were observed in the partly-carbonated zone – some oriented parallel to the carbonation front, and some perpendicular to it. The shrinkage cracks subsequently fill with secondary carbonate. The ultimate product after carbonation was a matrix filled with a meshwork of $CaCO_3$, finely nano- to micro-crystalline $CaCO_3$ and an amorphous Si-rich gel phase and Al-rich material.

The mineralogy of the $CaCO_3$ showed spatial (and possibly temporal) variation. Close to the main reaction front (i.e. where it was first precipitated) it occurred mainly as aragonite and vaterite. However, calcite was increasingly dominant with distance from the reaction front (i.e. where the sample had been carbonated for longer times). This demonstrates another potential complexity of cement carbonation that could be included within numerical models of cement carbonation – even though it remains unclear whether these observations reflect a slow conversion of less stable aragonite or vaterite to more stable calcite over time, or secondary phase control by differences in the local chemical environment.

In terms of uncertainties, the intermediate zone of partial carbonation was very variable in width, ranging from μm to several mm wide. The reason for this variability is not clear. A second area of uncertainty is cement matrix/fabric heterogeneity. For example, a few of the cement samples displayed a strongly grain-size differentiated layered fabric, which was on a similar length scale to the samples used. This appears to be artefact of cement casting, producing coarser and finer layers, with hydro-dynamic segregation of bands of limestone-rich grains and coarser cement

clinker. The coarser layers were associated with concentrations of limestone aggregate and coarsely-crystalline $Ca(OH)_2$ cement filling the coarser pore space, whereas the finer laminations were dominated by CSH. CO_2 preferentially altered the $Ca(OH)_2$ bands, resulting in uneven alteration and a 'stripy' appearance of some reacted cores (Figure 5). However, this did not change the nature of secondary phases produced. Whilst unwanted in these experiments, such heterogeneity has the potential to form within actual repository cement, though the use of additives to inhibit dewatering or grain segregation would help prevent its formation.

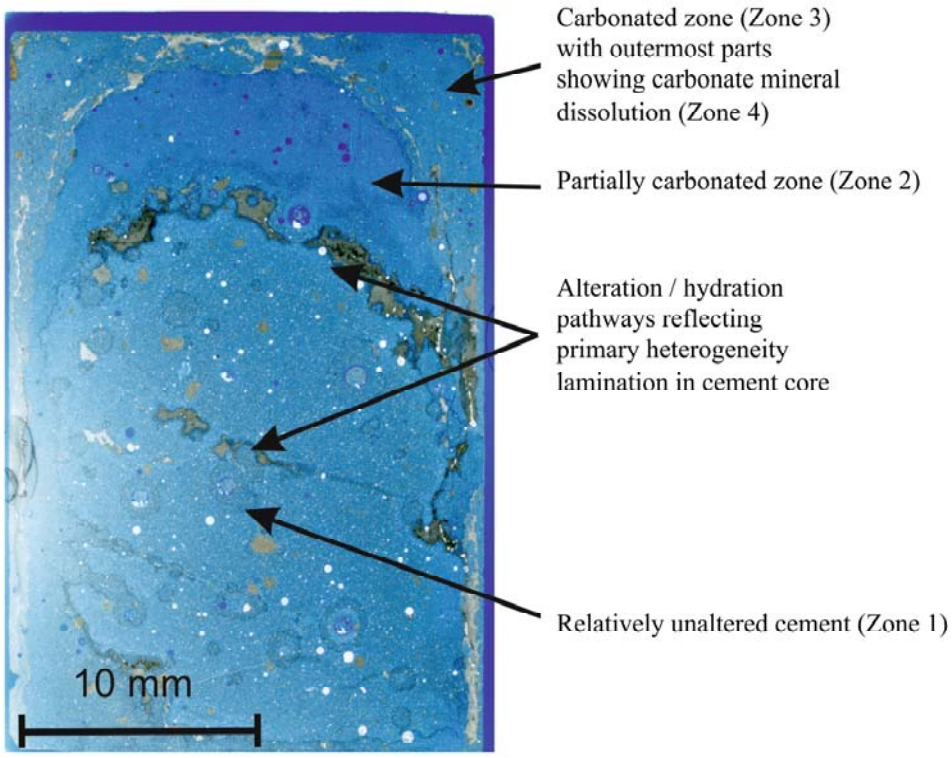


Figure 5 Transmitted light image of polished thin section through core of NRVB reacted with 'YNFP+Cl' in the presence of gaseous CO_2, 40 days at 40 °C under 40 bar pressure. Top and sides of image represents outer edges of the cement core. Patterns or pathways of changes in hydration and alteration in the relatively unaltered cement are influenced to some extent by pre-existing heterogeneity (particle size segregations / laminations) in the original cement.

Fluid chemical changes

Chemical changes in aqueous fluids in contact with NRVB cement were determined for most of the static batch experiments and only a subset are shown here (see Rochelle et al., 2014 for the full dataset). Prior to describing some of the more noteworthy results, it is important to note that most, if not all, of the experiments had not reached full chemical equilibrium. For example, whilst the outer parts of the cement samples may have been in equilibrium with the surrounding fluids, the central parts of the cement samples were still undergoing reaction. Thus, some dissolved species may have attained steady-state concentrations and have been in equilibrium with stable secondary phases, whilst others were still increasing in concentration. Reaction kinetics and the rate of transport of dissolved species through the cement are thus important considerations in assessing overall cement reactivity. Running experiments for different timescales provides some information as to whether steady-state concentrations had been achieved, with the 12-month long experiments being closest to full equilibration in this study. The maximum duration of the latter was constrained by the duration of the FORGE project.

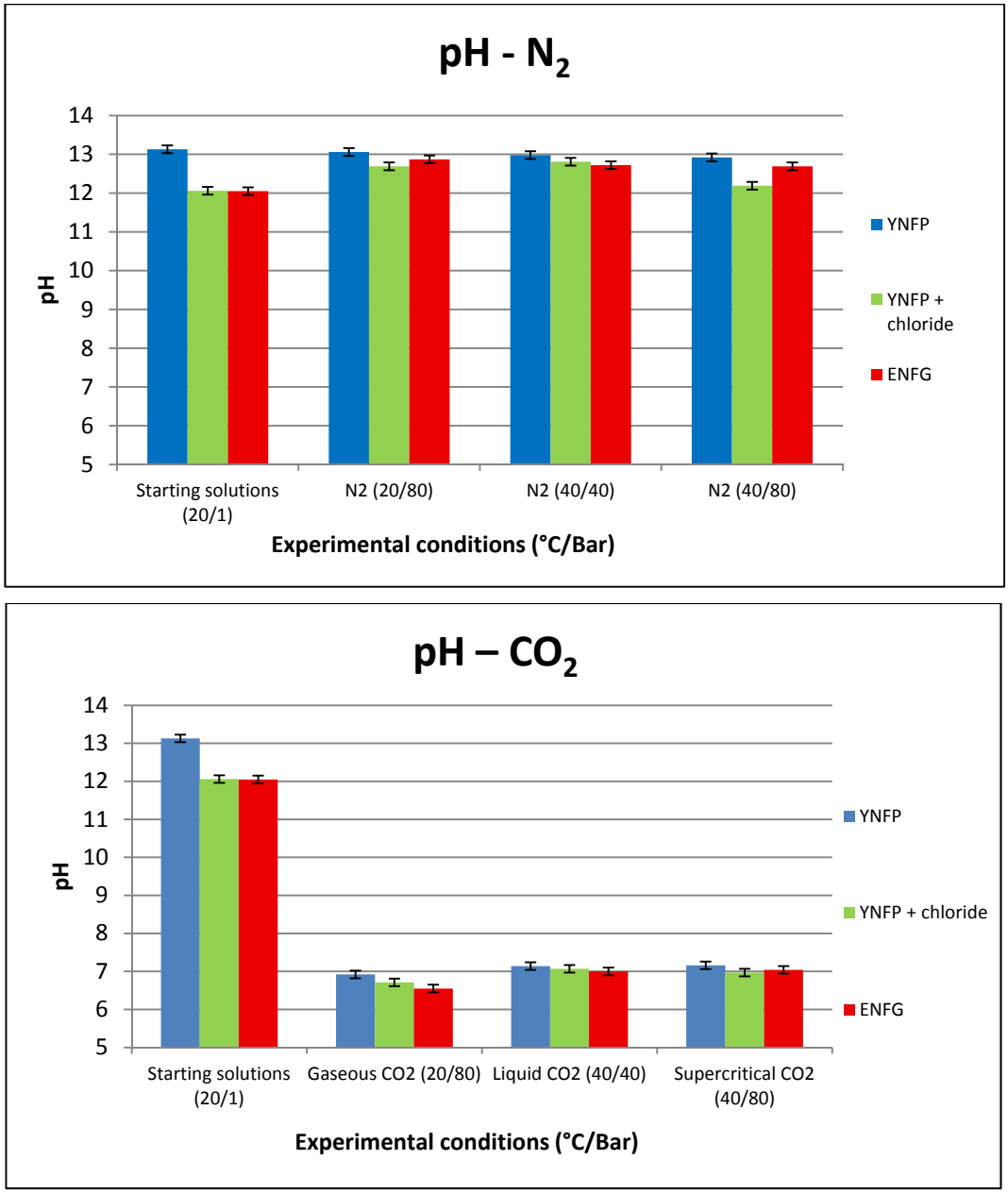


Figure 6 Changes in pH during the 40 day experiments (as measured at room temperature and pressure). Upper graph - nitrogen experiments, lower graph - CO_2 experiments.

Comparison of data from experiments of the same duration provides information on the *relative* changes in fluid chemistry under different conditions.

In the absence of CO_2, the pH of solutions in contact with the cement attained values of 12-13 expected for cement-equilibrated waters. However, the pH of the solutions showed a marked decrease on the addition of CO_2 (Figure 6). This observation mirrors those from previous studies where CO_2 was reacted with samples of cement used to seal the gaps between steel borehole linings and the surrounding rocks (Rochelle et al., 2004, 2006, 2007). Note that *in-situ* pH would have been lower than those measured on cooled and depressurised samples. This applies in particular to the CO_2-rich waters, which underwent extensive degassing of CO_2 on sampling.

As the CO_2 was present in excess, it would have provided the dominant control of pH. This can be represented by a series of reactions; first CO_2 dissolution, then reaction of CO_2 with water, and finally neutralisation of hydroxyl ions:

$$CO_{2(g)} \Leftrightarrow CO_{2(aq)} \qquad [4]$$

$$CO_{2(aq)} + H_2O \Leftrightarrow HCO_3^- + H^+ \quad [5]$$

$$OH^- + H^+ = H_2O \quad [6]$$

Subsequently the rate of this reaction would have been dictated by the rate of production of OH^- (or H^+ consumption) by the sample of cement. A consequence of these reactions is an increase in concentration of dissolved bicarbonate. This illustrates the potential for CO_2 to impact the high pH buffering capacity of the cement, and also to increase the concentration of potentially complexing ions in solution.

The two most important phases in cement (portlandite and CSH phases) are both Ca-rich, and led to a significant concentration of Ca in solution (Figure 7). The trends in dissolved Ca are more complex than for pH, as Ca solubility is a function of temperature, fluid composition and CO_2 concentration. For example, in the absence of CO_2 warmer conditions led to increases in Ca concentration for the 'young' porefluids, but lower concentrations for the 'evolved' porefluids.

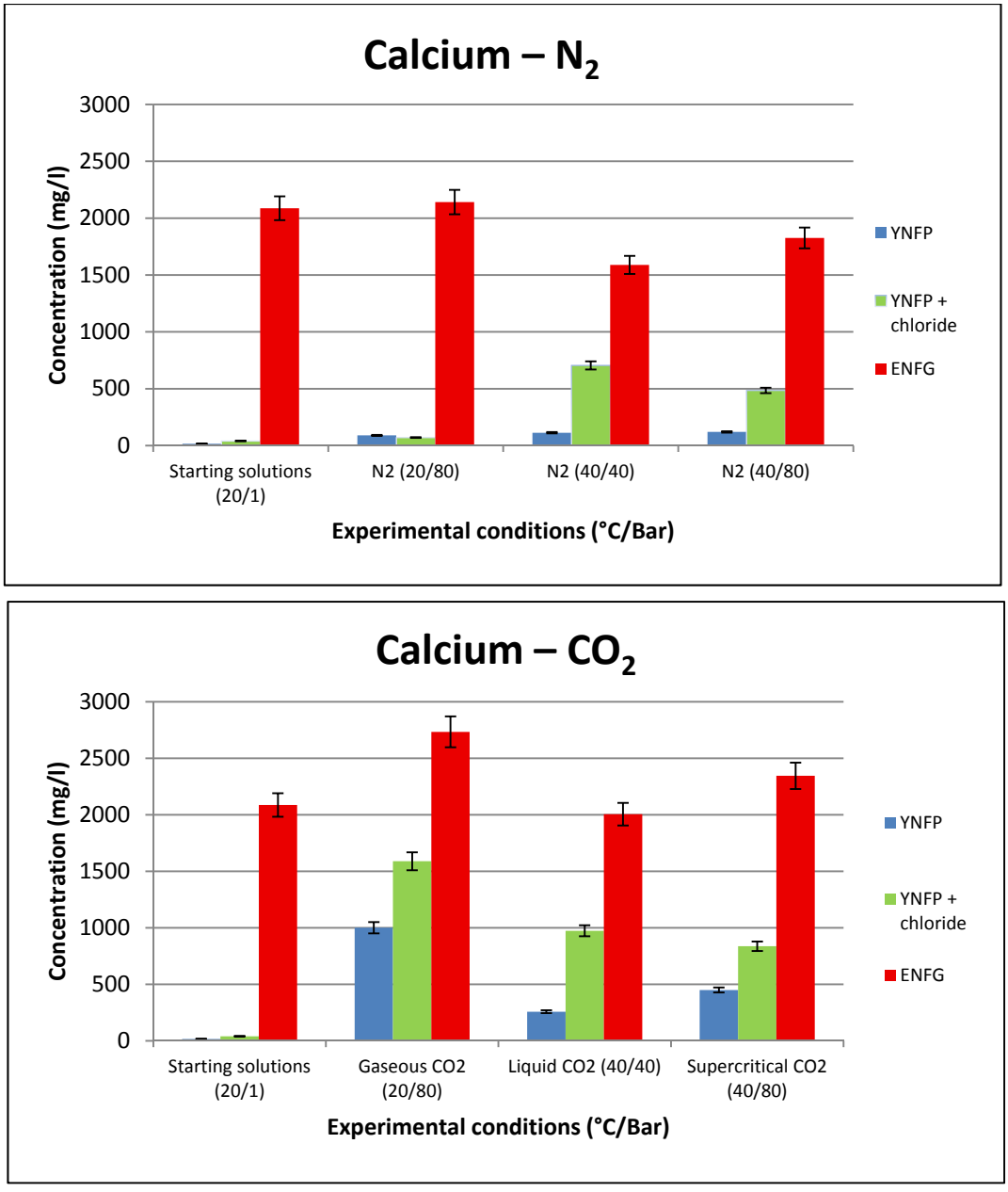


Figure 7 Changes in Ca concentrations during the 40 day experiments. Upper graph - nitrogen experiments, lower graph - CO_2 experiments.

What is clearer however, are the increases in dissolved Ca concentrations in the presence of CO_2, and this reflects dissolution of phases within the cement. In the presence of CO_2, the phase controlling Ca solubility was most likely calcite, rather than portlandite or CSH phases as in the CO_2-free (nitrogen-pressurised) experiments.

Further evidence for dissolution of cement components can be seen in the silica concentration data (Figure 8). These are mostly much higher in experiments containing CO_2. The lack of data in Figure 8 for the nitrogen-pressurised experiments reflects concentrations below the detection limits of the analytical technique used, and the mutual exclusivity of dissolved Ca and silica can be explained by equilibration with a CSH phase. The presence of significant Ca and silica in the CO_2 experiments also suggests that the solution is no longer equilibrated by CSH phases – the outer parts of the cement having reacted. The source of silica in the CO_2 experiments would have been dissolution of CSH phases. The broad consistency of the concentration of dissolved silica at 40°C suggests equilibrium with a common secondary Si phase, which in this case is likely to be silica gel formed through the carbonation of CSH (see reaction [2]).

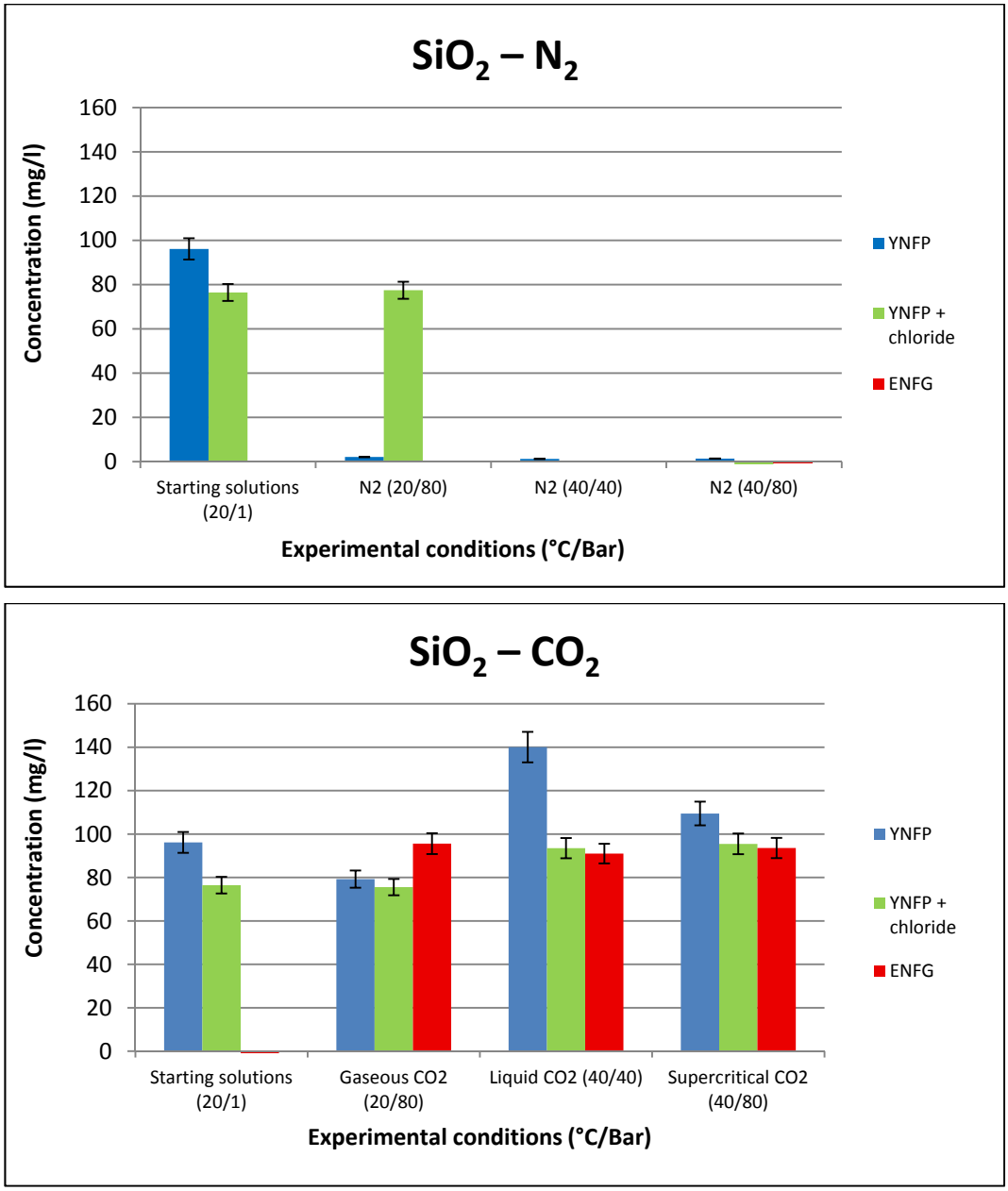


Figure 8 Changes in SiO_2 concentration during the 40 day experiments. Upper graph - nitrogen experiments, lower graph - CO_2 experiments.

2.2 FLOW EXPERIMENTS

The aim of these experiments was to investigate changes in flow properties of NRVB cement in response to ingress of gaseous, supercritical and dissolved CO_2. This was achieved by confining the cement test sample, forcing an advective flow through the sample, and carefully monitoring inlet and outlet flow rates and pressures. These results were then used to calculate flow properties. Details of this work are described in Purser et al. (2013a,b).

The same NRVB cement was used as in the static batch experiments, but this time it was sub-cored to produce samples of 49 mm diameter x 49 mm long. The small cylindrical samples were sandwiched between sintered filters (to facilitate fluid distribution) and stainless steel end caps. A Teflon jacket was used to exclude the confining fluid. Volumetric flow rates into and out of the samples were controlled and monitored using a pair of ISCO-500HP, series D, syringe pumps operated from a single digital control unit linked to remotely operated LabViewTM software (Figure 9). Data collection was performed every 2 minutes with a sub sample of this data being used for analysis. The tests were performed inside an oven at 40 °C. All samples were isotropically confined at 4 MPa above pore pressure. Four main tests were conducted:

1) Partial carbonation using CO_2 gas (NRVB-1) at 40°C and 40 bar
2) Full carbonation using CO_2 gas (NRVB-2) at 40°C and 40 bar
3) Full carbonation using supercritical CO_2 (NRVB-4) at 40°C and 80 bar
4) Full carbonation using water saturated with gaseous CO_2 (NRVB-5) at 40°C and 40 bar

A typical test history comprised of a sequence of test stages, each designed to quantify the hydraulic and gas transport properties of the cement. A single experiment therefore, could provide information on pre-carbonation hydraulic and gas permeability, plus post carbonation permeability.

Initially, injection and backpressure pumps were filled with $Ca(OH)_2$-saturated water to re-equilibrate the sample after initial assembly. Use of this fluid minimised the potential for portlandite leaching from the sample. Once complete, hydraulic testing commenced by increasing and decreasing the injection flow rate in a stepwise manor, doubling and halving the flow rate from 2125 µL/hr to 8500 µL/hr. N_2 and CO_2 injection tests then proceeded; N_2 to

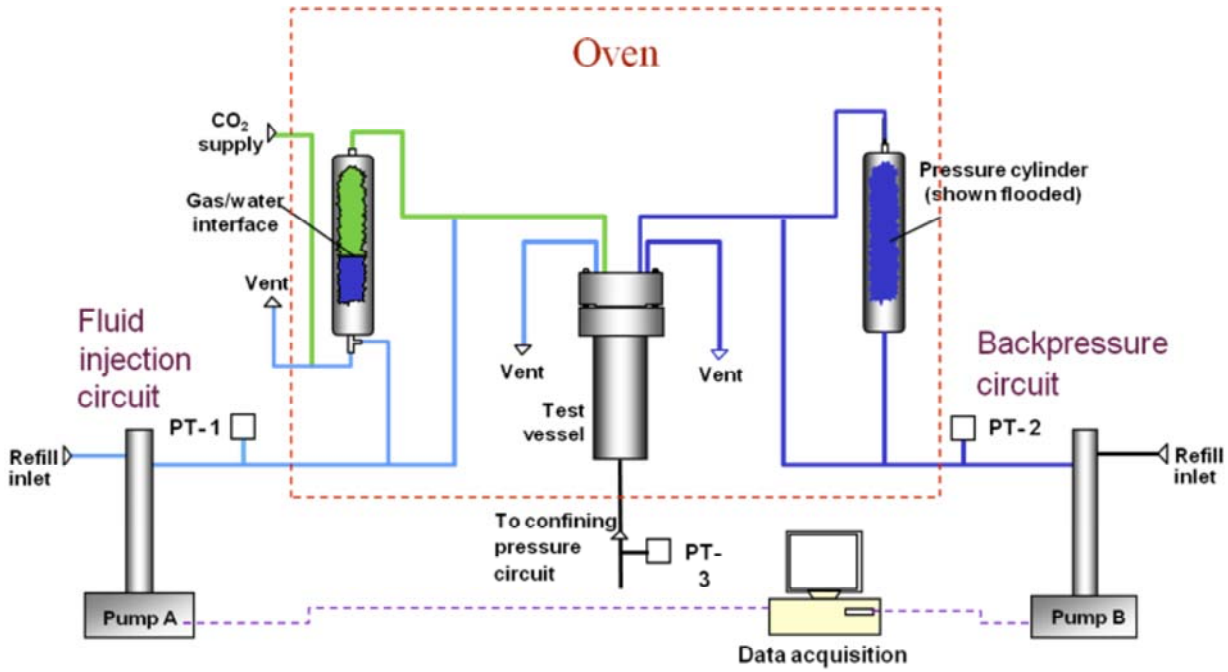


Figure 9 Schematic diagram of the flow test equipment.

Test	Initial hydraulic permeability (m^2)	Hydraulic permeability after aqueous CO_2 injection (m^2)	N_2 gas permeability (m^2)	CO_2 permeability (m^2)
NRVB-1	4.3×10^{-17}	-	N/A	N/A
NRVB-2 before N_2	4.1×10^{-17}	-	-	-
NRVB-2 after N_2	4.2×10^{-17}	-	2.20×10^{-19}	-
NRVB-2 after CO_2	-	-	1.13×10^{-19}	1.00×10^{-19}
NRVB-4	4.0×10^{-17}	-	-	1.94×10^{-19}
NRVB-5	4.7×10^{-17}	4.28×10^{-20}	-	-

Table 2 Summary of average permeability data from the NRVB cement carbonation tests.

provide baseline data for an inert gas, and CO_2 to carbonate the sample. Where appropriate, a second N_2 gas test was undertaken after sample carbonation.

NRVB 1: Partial carbonation test with CO_2 gas

The hydraulic tests showed unaltered NRVB cement to be relatively permeable (Table 2). Previous studies of NRVB flow properties used deionised water (Francis et al., 1997), and report a slightly higher permeability coefficient of around 1×10^{-16} m^2. It is thought that the use of deionised water in this earlier work may have caused some dissolution of phases within the NRVB. As a consequence, this may have resulted in artificially high porosity and permeability in the samples, and this may help explain the differences between our results and those of Francis et al. (1997).

On addition of CO_2 gas, injection pressure increased, indicating permeability reduction. For this first test, only a limited amount of CO_2 was injected in order to investigate the carbonation front within the sample. As a consequence, steady-state flow conditions were not reached during the experiment, preventing calculation of gas permeability. An assessment was made of the amount of carbonation using an acid digestion method, with 19.5 g of CO_2 found to have reacted with 158.2g of NRVB cement. This is comparable with the measured amount of CO_2 injected using the high precision syringe pumps.

The partially-reacted cement core displayed an obvious wedge-shaped reaction front (associated with a marked colour change) that had propagated half way along the length of the core (Figure 10), and was investigated in detail. Small-scale variation in permeability along the sample length was determined using a N_2 micro-permeameter. These values are significantly higher than those for saturated NRVB quoted in Table 1 as these measurements were performed after the core had been subject to vacuum desiccation. However, the data provide an indication of the relative changes in permeability across the length of the sample. A reduction in permeability was observed within a narrow zone at the leading edge of the visible alteration front. This could account for the higher pressures generated during the CO_2 injection stage of later experiments. Dissolution of CSH phases and portlandite and leaching of calcium, are observed in a very narrow region in front of the leading edge of the carbonation. This is associated with enhanced microporosity in the same region. The calcium appears to have migrated towards the carbonation front where it is concentrated in a fine meshwork of carbonate precipitation (possibly representing filled microfractures). The carbonated zone was very similar to that found in the static (diffusion-controlled) experiments comprised a 3-dimensional ‘chicken wire’ meshwork of calcite-mineralised microfractures within a nanoporous matrix of amorphous silica and fine grained patchy replacive calcite, with disseminated remnants of brownmillerite from the original cement slag. Entrained air bubbles in the cement were also partially filled by vaterite.

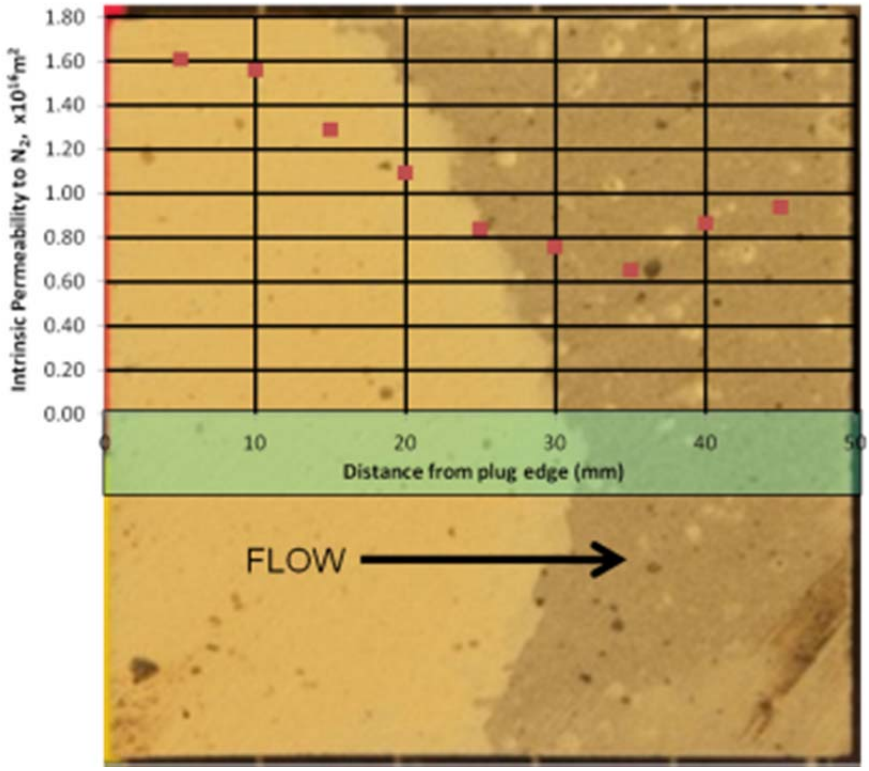


Figure 10 Photograph of the cut core of partly carbonated cement from flow test NRVB-1. Note the lighter coloured carbonated cement (to the left), thin reaction front, and the relatively unaltered cement (to the right). Micro-permeameter data show decreased permeability close to the reaction front.

NRVB-2: Full carbonation test with CO_2 gas

The hydraulic permeability data were found to be consistent with that of NRVB-1 (Table 2). Conductivity and permeability remained unaltered after the gas injection test with N_2, confirming its non-reactivity with NRVB. Maximum test pressures were significantly higher during CO_2 injection compared to those observed during N_2 injection. A marked breakthrough was signified by an increase in outflow after 22 days, and this continued until steady state conditions were achieved. Major gas breakthrough lagged behind the pressure peak, probably reflecting the complexity of the reaction fronts. Pre- and post-carbonation gas tests (using N_2) clearly show a change in permeability leading to increased gas pressures observed (Table 2).

NRVB-4: Full carbonation test with supercritical CO_2

The initial hydraulic permeability data were again found to be consistent with that of NRVB-1 (Table 2). Permeability data post-carbonation for supercritical CO_2 show a small reduction in permeability that is broadly similar to that for gaseous CO_2 (test NRVB-2).

NRVB-5: Full carbonation test with dissolved gaseous CO_2

This test was different to the other flow tests in that CO_2 was added to the cement core in solution. The dissolved CO_2 was prepared at pressure by reacting cement-equilibrated water with an excess of high pressure CO_2, and then filtering out the extensive $CaCO_3$ precipitate that had formed. As the CO_2 was only dissolved, it was effectively added to the cement at a much lower concentration compared to the tests involving free phase gaseous and supercritical CO_2. It was immediately apparent that pressures increased upon carbonation (at a constant flow rate), and

that flow paths within the cement blocked up rapidly. This resulted in an approximate 3 orders of magnitude decrease in hydraulic permeability (Table 2). Dissolved CO_2 therefore appears to be very efficient in reducing cement permeability. That said, this probably requires an excess of cement to be present, as *prolonged* exposure to a *flow* of acidified CO_2-rich water to carbonated cement will start to dissolve the initially-precipitated carbonate phases.

Mineralogical changes

Carbonation of NRVB cement samples during the flow tests resulted in similar mineralogical changes to the static batch experiments, plus the formation of reaction fronts that travelled through the samples. Portlandite and CSH phases were destroyed, and $CaCO_3$, silica, iron oxides/hydroxides and aluminium oxides were formed. This process is associated with localised porosity increases, which are then variably filled with secondary $CaCO_3$. As the reaction front travelled through the sample, a tight zone of significantly reduced permeability was created. This has the ability to 'armour' some regions of the cement, leading to isolated islands of unreacted NRVB and so reducing its total buffering capacity. Overall bulk gas permeability is reduced on carbonation. While this behaviour may not adversely affect the transport behaviour of NRVB, further work is required to fully understand the complex coupling between fluid flow, permeability and carbonation.

2.3 MODELLING ADVECTING CO_2-CEMENT REACTION

The PRECIP reaction-transport code (Noy, 1998) was used to produce an initial numerical representation of the cement carbonation experiments. This 1D code couples fluid transport to chemical reaction, and takes account of both changing porosity/permeability and mineral dissolution/precipitation rates. The code considers only a single phase fluid, and is thus a closer representation of dissolved CO_2 flow experiments (experiment NRVB-5 described above). Whilst it cannot represent the injection of high pressure gas into an initially water saturated sample, its use may help understand some of the factors that control the system in the gaseous and supercritical CO_2 flow experiments. Details of this work are described in Purser et al. (2013).

A simplified cement composition was used, which was represented as a mix of tobermorite, calcite and portlandite, with a porosity of 52%. The pore fluid in the cement was assumed to be initially at equilibrium with this mineral assemblage. The simulation involved fluid injected into one face of the core sample, and that fluid comprised pure water equilibrated with calcite and CO_2 at 4 MPa. The base case calculation assumed a large total reactive surface area (10^6 m^2/m^3) and relatively large reaction rate constants. The surface areas of the initial components within the cement were approximately in proportion to their volumes. The simulated fluid injection rate was $3x10^{-7}$ m^3 m^{-2} s^{-1} (2 ml hr^{-1} for a 49 mm diameter core), which generated a porewater velocity of $5.8x10^{-7}$ ms^{-1}. For a 49 mm long core this represented an injection rate of approximately 1 pore volume per day. This combination of injection and reaction rates created a short reaction zone, about 9 mm long, that progressed stepwise along the cement core. The prediction of a reaction zone is noteworthy, as it mirrors what was seen in the experimental reaction products (albeit that they were of slightly different thickness). The use of a code employing purely equilibrium chemistry would have resulted in a very sharp reaction front and no prediction of a reaction zone. The model predicted the complete transformation of tobermorite to aragonite and silica (represented by chalcedony in the model), followed by slower transformation of silica to quartz, and of aragonite to calcite. Additionally, there was gradual dissolution of portlandite adding to the generation of aragonite. A small net reduction in porosity was predicted, except near the inlet end of the core where the aragonite started to re-dissolve. The pH of the outlet fluid remained high until the reaction zone reached the end of the core.

The initial calculation was repeated with the dissolution rate of tobermorite reduced by a factor of 2.5, as were the precipitation rates for chalcedony and aragonite. The effect of this change was to increase the length of the reaction zone to about 20 mm. This demonstrates the sensitivity of the size of the reaction zone to mineral reaction rates. Shown in Figure 11 are plots of changing pH and porosity over time for this simulation, and of mineral abundance and Ca^{2+}/HCO_3^- concentrations after 100 hours of simulated time. It should be noted that the pH plots for 50 and 150 hours in Figure 11 are overlain by the plots for 100 and 200 hours respectively as a result of the stepwise progress of the reaction zone.

Noticeable in both base and reduced rate models are the spikes in aragonite precipitation at the end of each reaction zone step with corresponding reductions in porosity (Figure 11). The aragonite spike occurs just at the end of the tobermorite dissolution zone. The Ca^{2+} concentration drops to near zero at this point, but then rises again due to the dissolution of portlandite. The predicted gradient in Ca^{2+} concentration drives diffusion of calcium back against the porewater flow providing material for the excess aragonite precipitation at discrete intervals. Back-diffusion of Ca^{2+} concurs with conclusions based upon observations of the reaction front from experimental materials and previous studies (Rochelle et al., 2014). However, the narrow zones of carbonate precipitation are on a cm-scale in the model, but at sub-mm scale in the experimental samples. Adjusting parameters in the model could probably produce a closer match to that observed in the experiments, though this would require more refined, much finer gridded models to better represent the complex interplay between diffusion, mineral reaction rates, mineral saturation and fluid flow rates.

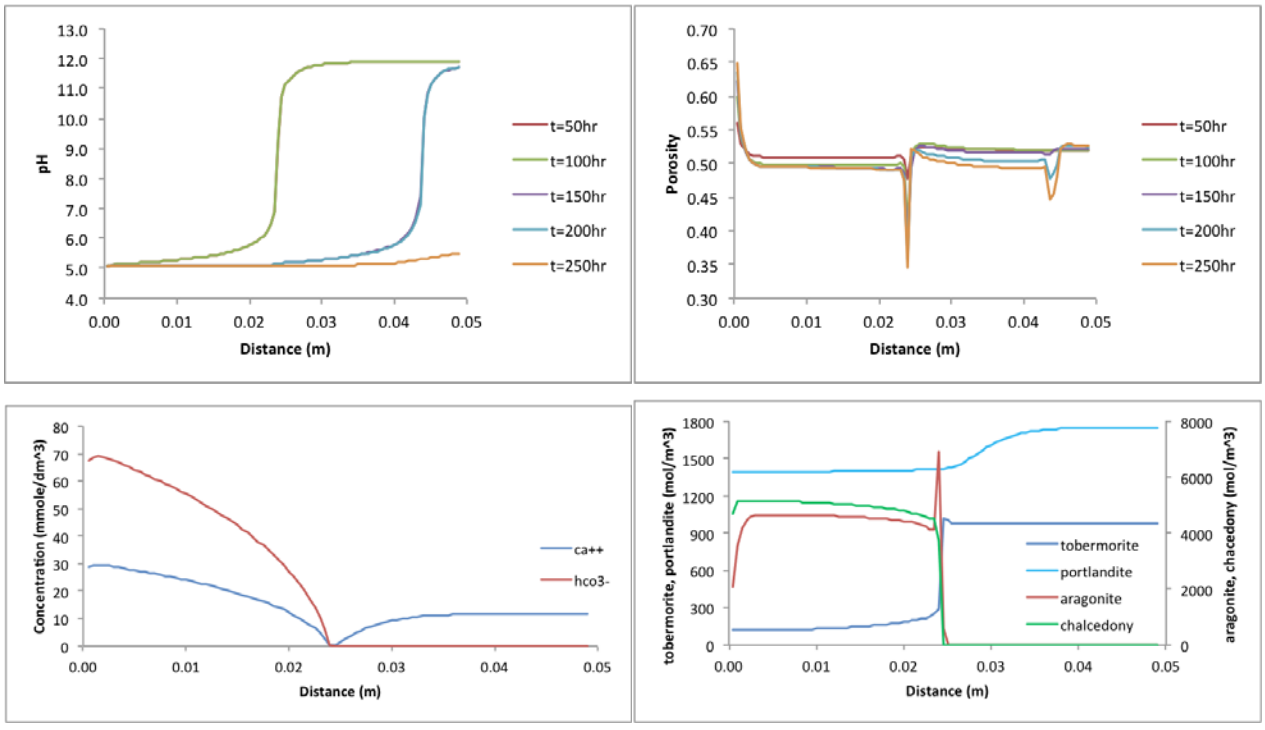


Figure 11 Mineral, porosity and aqueous concentrations at 100 hours of simulated time for the 'reduced dissolution rate case' (see Purser et al., 2013).

3 CO_2 transport mechanisms

In a repository setting, CO_2 could be present in dissolved form (as $CO_{2(aq)}$, HCO_3^-, CO_3^{2-} or complex ions depending upon local fluid chemical conditions), but if enough of it were generated to exceed saturation then it could also be present as a free phase. In terms of transport mechanisms therefore, it could migrate as:

- Diffusion of dissolved species along a chemical gradient.
- Downward advection of dissolved species due to density increase of water upon CO_2 dissolution (e.g. Kneafsey and Pruess, 2010; Pau et al., 2010).
- Advection of free-phase CO_2 along a pressure gradient, or buoyant upward advection.

In this investigation, we studied the impacts of CO_2 diffusion on NRVB cement via static batch experiments. The work focussed on the formation of chemical reaction fronts and the ensuing mineralogical and textural changes, rather than on measuring diffusion rates. The impacts of CO_2 advection were studied via flow experiments. These included flow of dissolved and gaseous CO_2 (being the more likely forms in a future repository setting). However, we also investigated the flow of supercritical CO_2 to scope cement reactivity under more extreme conditions.

The nature of CO_2 migration within the NRVB cement was also controlled to some extent by chemical reaction, a process that might not be apparent for other gases in different repository concepts (e.g. hydrogen migration through bentonite). Thus for example, CO_2 consumption through the formation of secondary carbonate minerals would set up steeper chemical potential gradients, enhance the apparent rate of diffusion, and possibly lead to faster migration of carbonate reaction fronts. Conversely, the formation of secondary carbonate minerals could block porosity, leading to significant reductions in permeability in the flow experiments. In terms of overall migration of CO_2 within cementitious systems therefore, it is necessary to consider chemical reaction, reaction kinetics and transport.

The aims of this study did not include quantification of diffusion properties. However, we were able to track the net effect of diffusion-controlled carbonation via the progression of carbonation fronts as a function of time. It should be noted that the fronts do not record the position of the leading edge of CO_2 ingress, as minor amounts of CO_2 reacted with cement in advance of the fronts. Instead, the carbonation fronts record the position where sufficient CO_2 had permeated the core to enable enough carbonation to occur to change the structure of the cement (including *complete* carbonation of the reactive cement minerals). The fronts migrated by a few mm over several weeks (Figure 12). However, the data from several of the 40 day long experiments show quite variable degrees of ingress of the carbonation fronts. Whilst some of the 40 day data are broadly in line with extrapolation of the 10 and 20 day data, some samples showed much slower ingress of the reaction fronts into the samples. We are unsure why this was the case, though sub-sampling from a heterogeneous cement block may have resulted in experimental samples of slightly different properties, and this might be one explanation.

Whilst many of the samples used in the static carbonation tests showed relatively uniform carbonation when sectioned, some displayed carbonation focussed along specific zones. These appear to be regions made from coarser grains, with the coarser porosity infilled by $Ca(OH)_2$. These were more reactive to CO_2 than the surrounding, finer-grained CSH-rich regions, resulting in non-uniform, complex reaction fronts. The cause of the original differences most likely relates to differential sedimentation of grains during the pouring and setting of the cement. The overall effect is to introduce a degree of uncertainty in the average position of the carbonation fronts, as different samples were affected to different degrees (i.e. small sub-cores from one part of the original large cylinder of cement may be affected, whereas others will not). That said, only a few of the samples used for the static tests showed these features, and none of the samples used for the flow tests appear to have been affected. The addition of certain (usually organic) additives to the cement may be one way to minimise differential sedimentation, but these additives may have

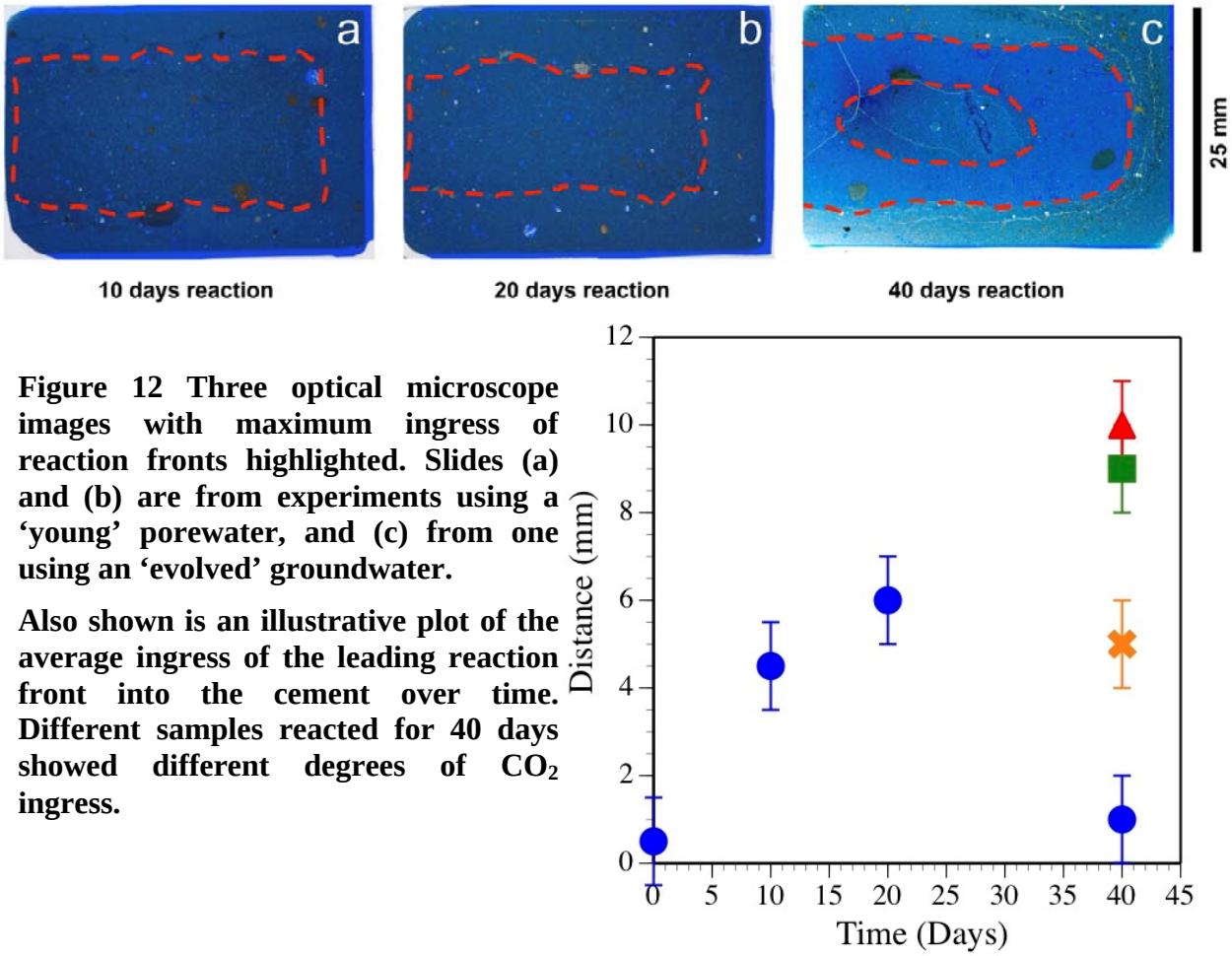


Figure 12 Three optical microscope images with maximum ingress of reaction fronts highlighted. Slides (a) and (b) are from experiments using a 'young' porewater, and (c) from one using an 'evolved' groundwater.

Also shown is an illustrative plot of the average ingress of the leading reaction front into the cement over time. Different samples reacted for 40 days showed different degrees of CO_2 ingress.

deleterious effects on the solubility and sorption behaviour of some radionuclides and thus be unwanted components within a repository (Francis et al., 1997). It is therefore possible that differential sedimentation may be a feature of additive-free NRVB cement in a repository, and that diffusional transport may result in regions of carbonation having complex shapes.

Experiments using an advective flow of CO_2 resulted in relatively uniform alteration of the cement, with no preferential alteration along specific zones. Injection of CO_2 was along the central axis of the core sample. As a consequence of the fast reaction of CO_2 and flow rate used, this resulted in a cone-shaped leading edge to the carbonated zone (Figure 10). As per the static (diffusion-controlled) experiments, a reaction zone was observed, though this was thinner in the flow experiments. Once the apex of the cone-shaped leading edge of the reaction front reached the outlet side of the cement sample it appeared to focus CO_2 migration. The net effect was to leave small areas of isolated unreacted cement close to the outlet end of the cement sample.

Flow in both the batch experiments (diffusion) and flowing experiments (advection) was via an open pore network. The NRVB cement is designed to have a very high permeability in order to allow gas migration and prevent excess pressures building up within a repository. Though some permeability reduction was observed in the laboratory tests, the carbonated cement still remained permeable to gas – though to a lesser degree. Whilst we recognise that the potential for excess gas pressures will also be governed by the rate of gas generation (including gases other than CO_2), based upon the results of this study there is no strong evidence to suggest that permeability will decrease sufficiently enough to allow excess gas pressures to develop (at least for realistic gas generation rates). It should also be recognised that CO_2 will be consumed by the cement through carbonation reactions, a process which will act to reduce gas pressures. As such, mechanical disruption of the NRVB cement seems unlikely, and consequently the potential for gas transport along newly-formed cracks appears unlikely.

There are however, two caveats to the above:

1) We cannot rule out the possibility that much slower carbonation reactions (i.e. at rates more realistic of a repository timescale) might produce narrower reaction fronts with more efficient infilling of porosity, and consequent larger reductions of permeability. These may serve as more effective barriers to CO_2 flow and allow higher differential pressures to develop. Indeed studies of naturally-carbonated, naturally-occurring CSH phases indicate that some reaction fronts can effectively 'armour' centimetre-scale nodules of CSH phases from further carbonation for several thousands of years (Milodowski et al., 2009; Rochelle and Milodowski, 2013).
2) As well as forming anastomising networks of 'chicken wire' fabrics, CO_2-cement chemical reaction occasionally caused two types of slightly larger, but still very *localised* temporary shrinkage cracks to develop (Figure 13). These were mm-scale features, located at the active carbonation front, and were only observed for unconfined samples in the batch experiments. One set of shrinkage cracks was oriented approximately parallel to the flow direction and the other set were approximately perpendicular to it. Each of the small cracks was only a temporary feature, as secondary precipitation eventually sealed these as the carbonation front progressed through the sample. Thus an individual pathway may be temporary, but a longer-lasting, narrow, 'dynamic' zone of potential flow pathways associated with the actual carbonation front appears to have slowly moved through the cement.

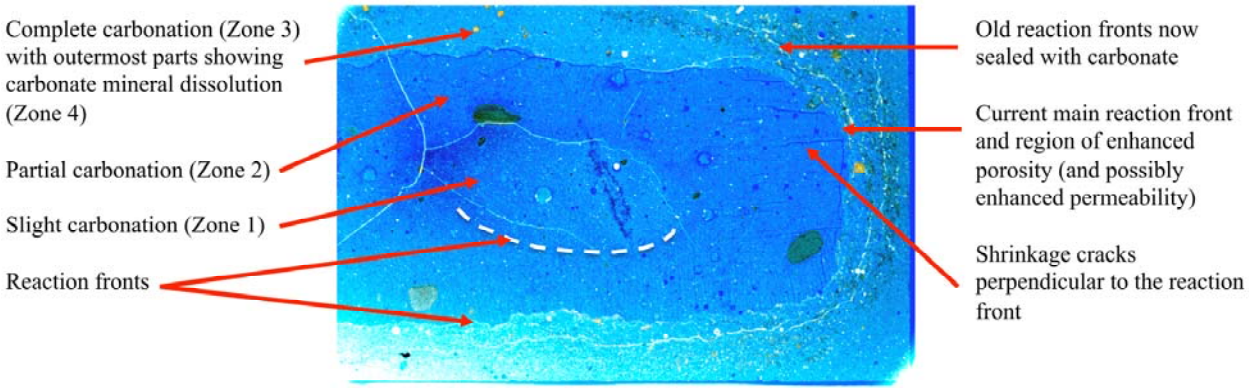


Figure 13 Partially carbonated cement sample showing zones having different degrees of carbonation together with associated reaction fronts.

Issues of gas transport through cement are of interest to other industries as well as radioactive waste storage. Several relate to hydrocarbon/CO_2 extraction, gas storage and the underground sequestration of CO_2. A key concern is the behaviour and sealing of cements that line boreholes and provide a seal between the surrounding rock and the steel borehole liner. Whilst the migration of gases such as methane will be mainly subject to physical control, CO_2 will react with the borehole cement. There are an increasing number of borehole cement carbonation studies, including laboratory tests, recovery of actual borehole samples, investigation of natural analogues, and predictive modelling (e.g. Carey et al., 2007; Milodowski et al., 2011; Rochelle and Milodowski, 2013; Wilson et al., 2011). Of particular concern is the potential for CO_2 transport along imperfectly-sealed interfaces between rock-cement and cement-steel. Whilst CO_2 extraction and enhanced oil recovery (EOR) schemes may only consider borehole lifetimes of a few tens of years, those concerning underground storage of CO_2 have to consider timescales of 10 ka to 100 ka – significant on a repository performance assessment timescale. Many CO_2-cement reactions and transport processes appear common to both CO_2 storage interests and radioactive waste disposal, even though the permeability characteristics of the cements may differ significantly.

4 The role of interfaces in CO_2 migration

Within a multi-barrier concept repository there will be many different interfaces between the repository components. It was not the aim of this study to investigate these interfaces, so only a few comments can be made about these. That said, our tests did *generate* interfaces between regions of partially-carbonated and fully-carbonation cements as a result of CO_2-cement chemical reactions. This resulted in shrinkage cracks and reaction fronts, which potentially could act as foci for fluid flow. Shrinkage could have resulted from water loss during carbonation, or actual solids volume decreases. There are indications that this localized zone of shrinkage and porosity enhancement migrates over time, with secondary carbonate precipitation progressively filling porosity after it is created. This secondary carbonate precipitation is also controlled by very local back-diffusion of calcium ions creating very narrow reaction/precipitation fronts. Thus a 'dynamic' zone of increased permeability appears to move through the sample, and is longer-lasting than one specific shrinkage crack.

Laboratory experimental studies and observations of boreholes as part of CO_2 storage studies have shown that imperfections in the sealing of steel/cement and cement/rock interfaces can have an important control on gas migration (e.g. Carey et al., 2007: Rochelle et al., 2009). For example, a poor steel/cement bond or an unsealed engineered damage zone (EDZ) at the cement/rock interface can allow CO_2 migration. Poor seals might also result from poor well management, or temperature cycling during periods of alternating production, injection, or shut-in. In the case of the study of borehole cement recovered from the SACROC Unit (Carey et al., 2007), zones of cement carbonation extended several metres up the well (i.e. into the overlying caprock) along the cement-rock interface (Figure 14). It is possible therefore, that if there was significant flow of acidic, CO_2-rich water along this interface, then there is potential to enhance dissolution and magnify interface permeability. On the other hand, significant dissolution will *only* occur if there is sufficient flow to remove dissolved components. In conditions of low or no flow, then reactions may occur initially, but once they approach local equilibrium will do very little thereafter. Indeed, if carbonation reactions resulted in a reduction in porosity/permeability and reduced potential for fluid migration, then they might improve the sealing of the cement. Cement carbonation therefore has the potential to be either beneficial or deleterious depending upon the specific environment and degree of reaction. Given the smaller amounts of CO_2 in the repository environment compared to CO_2 storage, and the larger (and potentially excess) amounts of cement, there would appear to be a relatively low risk that cement carbonation would cause major problems in the repository environment.

In terms of interfaces, CO_2 storage studies need to consider just those between steel/cement and cement/rock (e.g. Carey et al., 2007; Rochelle et al., 2009). Also, these interfaces may not be clean as they may be variably covered with drilling mud. Whilst residues from drilling fluids will not be an issue in a repository setting, it will however be important to consider cement/cement interfaces. These could occur, for example, between cement grout/backfill and concrete boxes containing steel drums of waste, between layers of grout/backfill if emplacement was staged, or between cavern structural cement and grout/backfill. There could also be chemical or mineralogical differences across the cement/cement interfaces – such as when different formulations are used, between different ages of cement (hydrated phases in cement becoming more ordered over time), or if some of the cement were exposed to higher than ambient temperatures due to the presence of heat-emitting waste.

There are other reactions that will also occur along interfaces. Carbonation reactions generate water as hydrated calcium silicate hydrate phases convert to carbonate minerals. If this water were to migrate towards grains of non-hydrated cement clinker, then new cement minerals may form (e.g. calcium silicate hydrates), and these may help lower local permeability. There are indications from a limited number of laboratory experiments undertaken as part of CO_2 storage studies (see Rochelle et al., 2009) that sealing along a cement-steel interface might actually

improve with ingress of *limited* amounts of water or CO_2, as this may result in new cement minerals growing and an improvement in sealing.

The behaviour of cement interfaces during carbonation is thus complex. However, one clear conclusion coming out of several CO_2 storage-related cement carbonation studies was that a high quality initial bond/seal was the best way to minimise gas migration. A good seal may actually improve with limited carbonation, but a 'leaky' seal is likely to get worse. Similarly, well-sealed interfaces will be needed in a repository setting.

Figure 14 Image of samples of borehole cement recovered after 30 years in a CO_2-rich environment (modified after Carey et al., 2007). Note that carbonation was focussed along the cement/steel and especially the cement/shale interfaces.

5 Upscaling from laboratory to repository scale

The experiments in this study were designed to simulate the potential upper and lower bounds of likely *in-situ* pressures and temperatures, and replicate specific scenarios as realistically as possible. We acknowledge however, that the experiments are relatively simple and have tightly-controlled conditions, and may therefore not replicate the complexities of 'real' systems. Also that there is a compromise in terms of timescales, as we were trying to simulate slow/low flow rate processes lasting 100s-1000s of years within a few months in the laboratory. Equally, we note that the sample sizes studied are far smaller than repository scale.

Upscaling of the processes identified by this study can be achieved by comparison with analogous systems. Whilst such systems may not have been studied in as much detail as the experimental samples of this study, they can provide information on temporal and spatial scales well in excess of those possible by experiment. Thus for example, in terms of physical size, for cement carbonation reactions there is very similar behaviour (qualitatively) with multi-metre scale observations of carbonated borehole cement from CO_2-production wells (e.g. Carey et al., 2007). Though the cement formulations may be different between those used as NRVB buffer-backfill and borehole seals, many of the phases involved and reaction processes appear similar in both cases. Though Carey et al. (2007) do note a degree of alteration of the bulk cement, their results clearly demonstrate the importance of interfaces (steel-cement, and cement-rock) in facilitating CO_2 migration, along which CO_2 moved several metres in 30 years.

Extension of temporal scales to several thousands of years is possible through the study of analogous systems. Thus for example, modern borehole cements have been in use for a few 10s of years, Portland-type building cements 10s to approximately l50 years, Roman cements approximately 2000 years, other building cements up to approximately 5000 years, and naturally-carbonated naturally-occurring cement minerals for timescales of 10000s to 100000s of years. In relation to the current study, broadly comparable observations have been made of material from; carbonated borehole cements (Carey et al. 2007 - reactions over 10s years), and naturally-carbonated cement minerals reacted for >1000s years (natural analogues, Figure 15) (Rochelle et al., 2007; Milodowski et al., 2009). The size and age of some of these analogous systems are much closer to those required for repository assessments, and the similarity between observations of laboratory experiments and analogues leads us to believe that we can successfully translate many of them to repository scenarios.

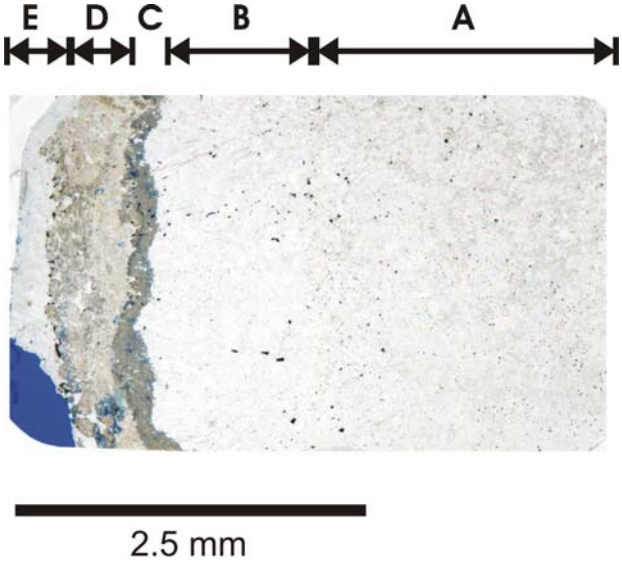


Figure 15 Transmitted light image of a thin section through an altered calcsilicate nodule. It shows zoned alteration: A - quartz-rich zone with minor larnite; B – larnite with minor spurrite or paraspurrite; C – Inner zone of the late-stage alteration rim, with secondary porosity highlighted by blue resin; D – zone of carbonation reaction with scawtite, amorphous silica and calcium carbonate; E – host marble. Sample MPLM802B, Scawt Hill, Northern Ireland (From Milodowski et al., 2009).

Whilst some processes may behave similarly over a range of temporal and spatial scales, there are some notable differences. One of these appears to be the thickness of the carbonation interface. In the laboratory samples carbonated as part of this project it was possible to observe several discrete reaction fronts within a broader reaction zone. However, studies of naturally-carbonated naturally-occurring cement-type minerals (e.g. Milodowski et al., 2009, 2011; Rochelle and Milodowski, 2013) show a very narrow, single reaction front between carbonated and non-carbonated regions. It is possible that these differences are a function of the complex interplay between a series of reactions having very different rates, and we do not underestimate the difficulty in comparing these systems because of the very different CO_2 partial pressures, state of the CO_2, cement composition, CO_2 ingress rates etc. Nonetheless, it does seem possible that differences in the relative rates of fluid flow and mineralogical changes have less of an impact as timescales increase, leading to narrower reaction zones over longer timescales. It is possible that these narrower zones may also become more efficient at sealing permeability. It would be useful to investigate further the permeability of the carbonation zones and how this changes over prolonged timescales.

6 Potential impact of CO_2 on repository safety functions

Information presented in the previous sections clearly demonstrates that carbonation of cement can alter its permeability. At microscopic scales carbonation results in a patchwork of high porosity/permeability domains enclosed by thin low porosity/permeability zones. At a somewhat larger (millimetric) scale, there was some evidence that unconfined samples could develop stress cracking close to the carbonation reaction fronts, though these features were very localised and could be filled by secondary carbonates as the reaction fronts moved through the sample. For larger samples (several cm in size), the net effect of carbonation is to reduce permeability - at least halving its original permeability.

Such reductions in permeability are beneficial in terms of containment as they would act to limit radionuclide migration. The NRVB cement used in this study is designed to be relatively permeable, so as to safely vent gas pressure build-up within the canisters. The reductions in permeability observed in the tests conducted here, still allow for some gas migration through the samples of cement, albeit at a reduced rate. As a consequence, it seems unlikely that carbonation would cause overly high gas pressures to develop in the waste canister or around its vent, and so the risk of mechanical disruption appears low. That said, dissolved CO_2 was particularly effective at reducing permeability (by about 3 orders of magnitude, compared to a halving for gaseous or supercritical CO_2). Around the vents of waste canisters there could therefore be different regions of carbonation having different permeability, depending upon whether they were carbonated under conditions dominated by predominantly dissolved CO_2 or free phase CO_2. Assessing which type of carbonation will dominate will require consideration of the complex relationships between gas generation rates, cement permeability, and rate of cement reaction.

Most of the carbonation observed was relatively uniform on greater than mm scales. However, a small number of (mainly diffusion) samples showed some evidence for carbonation along specific zones. These are thought to relate to differential settling during cement pouring and curing. Similar features could form in a repository setting, and could provide preferential routes for CO_2 migration if they occurred on a large scale. Such cement heterogeneity could be minimised through the use of organic additives to enhance cement flow behaviour. However, Francis et al. (1997) note that the presence of such organics may enhance the mobility of some radionuclides. It will be important therefore, to consider carefully the pros and cons of adding additives to repository buffer/backfill cement.

There is clear evidence that cement carbonation can result in a lowering of cement pH buffering capacity as many metallic radionuclides have low solubility under alkaline conditions, but higher solubility as pH decreases. Potentially therefore, carbonation may facilitate local radionuclide migration. That said, if as seems likely, the repository contained an excess of cement that was more than sufficient to react with all the produced CO_2, then overall pH buffering to alkaline conditions could still be effective for many parts of the repository.

It is anticipated that carbonation reactions would help immobilise ^{14}C if that were present. However, one less expected observation concerning solute migration was the enhanced localised uptake of dissolved chloride (Cl^-) by the cement. ^{36}Cl presents particular issues within repositories, due to its long half-life, ease of uptake into biological systems, and relative mobility in many settings. Uptake of Cl^- was most clearly revealed by significant decreases in dissolved Cl^- in the experiments using more ‘evolved’ porewater compositions (i.e. porewaters reflecting interaction between saline groundwater and the cement) (Figure 16).

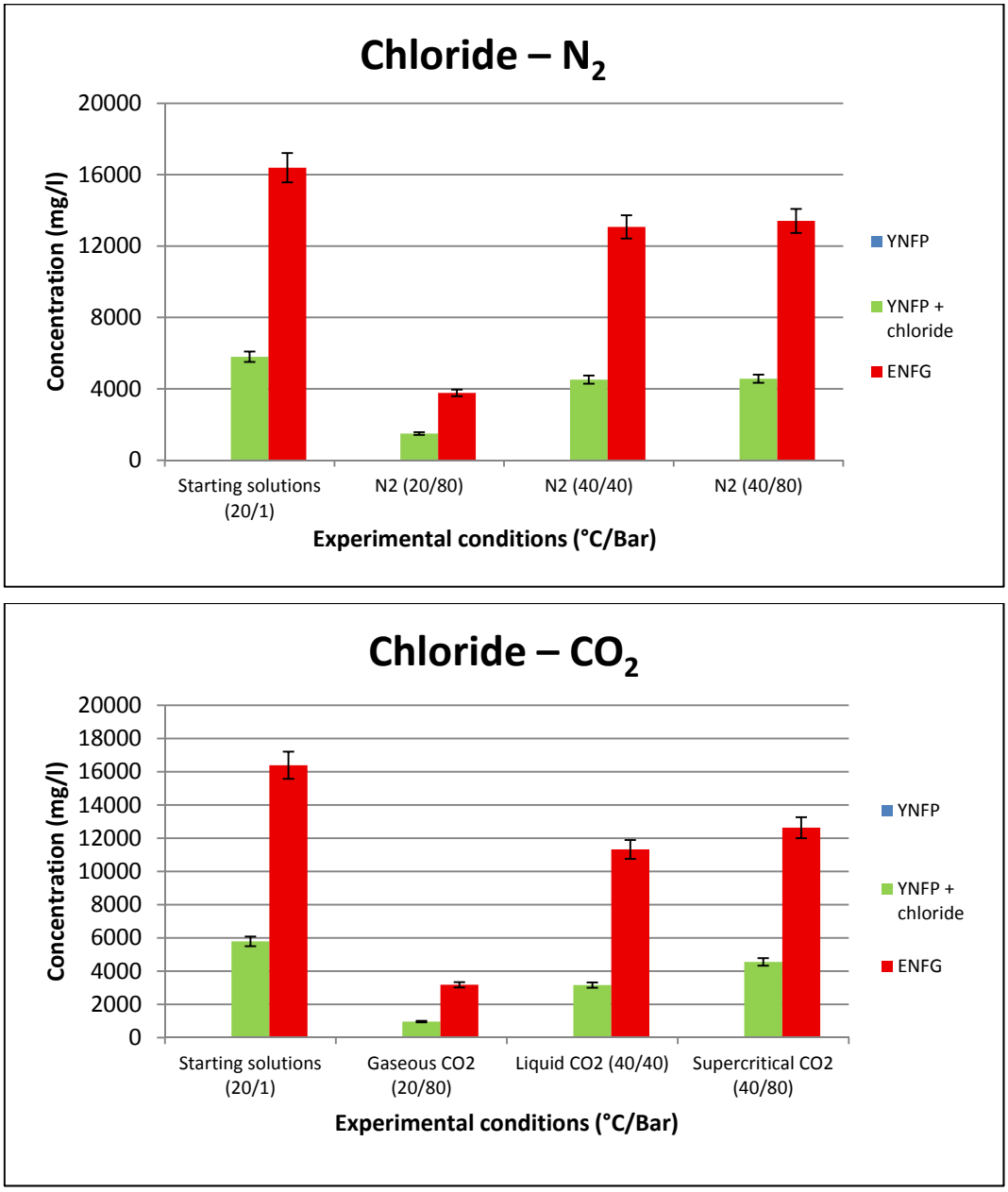


Figure 16 Chloride behaviour in 40 day static batch experiments. Note decreases relative to the starting solutions, especially at 20°C. Note also that concentrations in the YFNP experiments are too low to be visible on these plots. Upper graph - nitrogen experiments, lower graph - CO_2 experiments.

Many of the experiments showed decreases in dissolved Cl^-, not just those pressurised with CO_2. The NRVB cement appeared to be immobilising Cl^-, especially at lower temperatures (in this study 20 °C) where Cl^- uptake was especially favoured. Smaller, but still significant, amounts of *additional* Cl^- were taken up in equivalent experiments pressurised with CO_2. The additional stability provided by the presence of CO_2 possibly suggests that it may exist as part of a solid-solution series with Cl- and CO_3-endmembers.

Detailed mineralogical observations in the region around carbonation fronts revealed the presence of small amounts of two fine-grained, Cl-rich solid phases. One was a gel-like Cl-rich CSH, the other was only found in the 20 °C experiments and occurred as fine-grained radial fibrous crystal aggregates of a calcium chloroaluminate phase, probably hydrocalumite ($Ca_4Al_2O_6Cl_2.10H_2O$) (Rochelle et al., 2013; Milodowski et al., 2013) (Figure 17). Element mapping clearly showed that these Cl-rich phases were found on the cement-side of the reaction

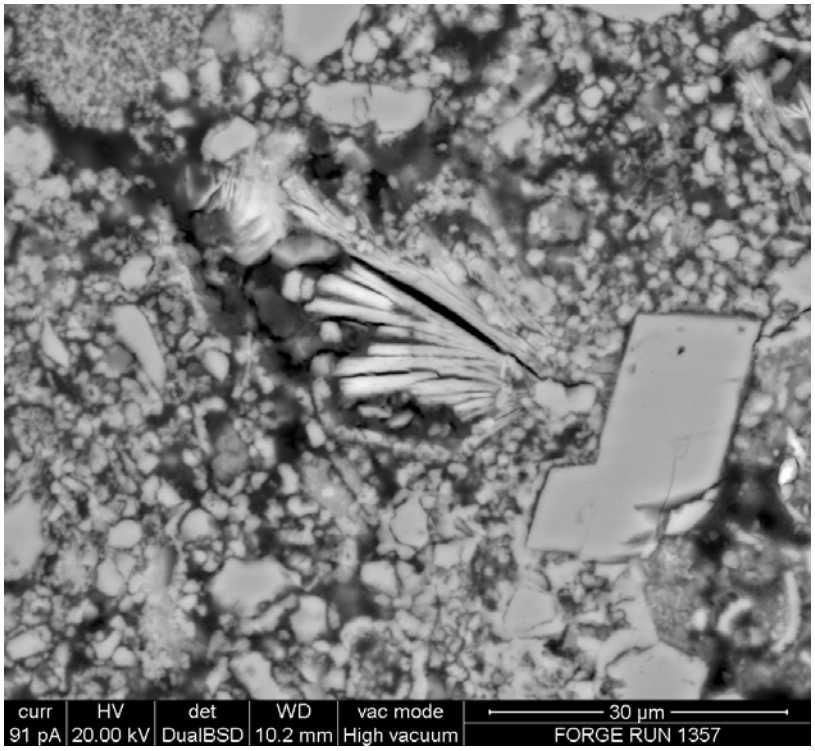


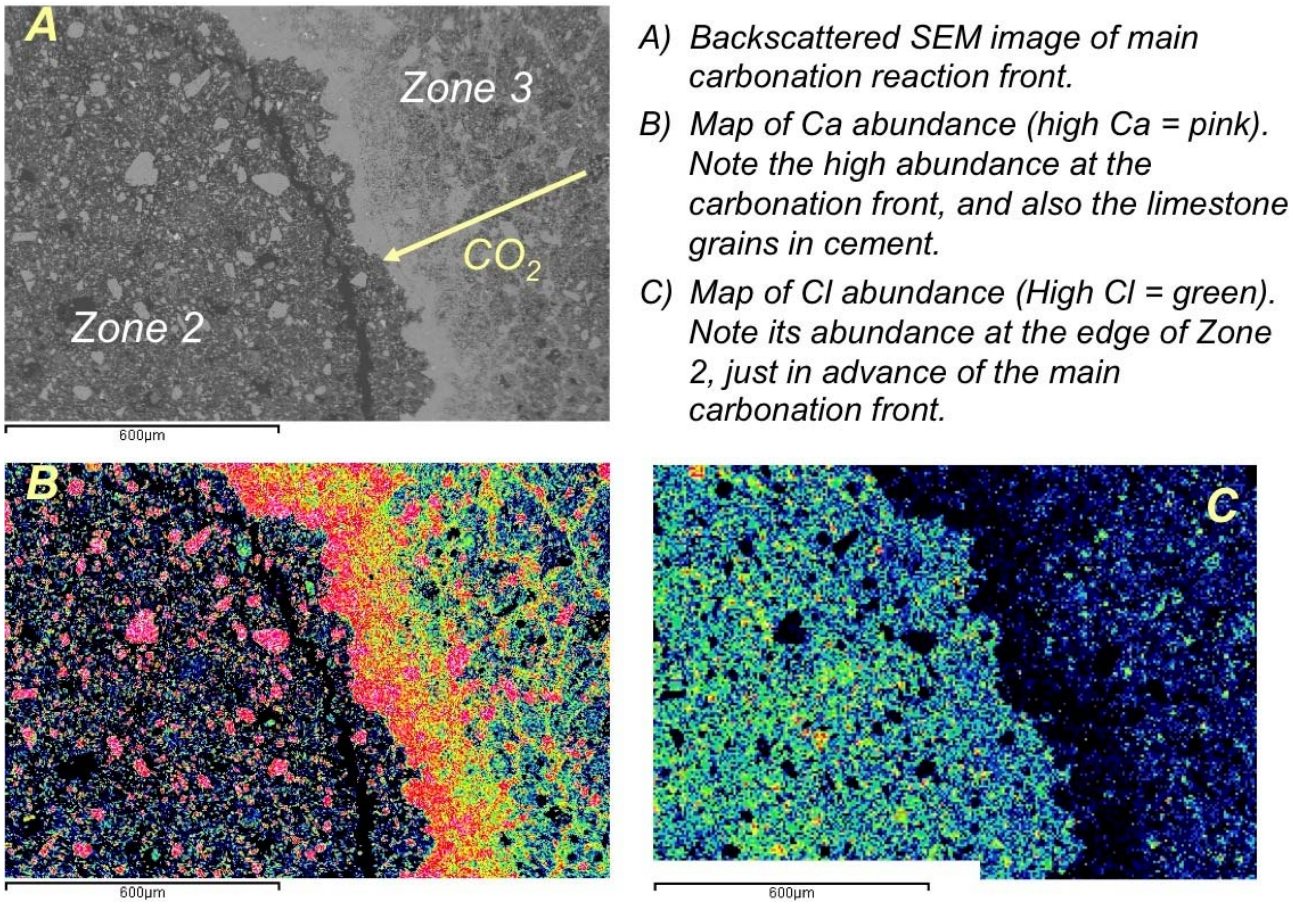
Figure 17 BSEM photomicrograph of radial fibrous secondary calcium chloroaluminate phase. This formed within altered cement just behind the leading edge of the carbonation front.

front (Figure 18). It would appear that they are only stable under higher pH conditions (i.e. where CSH phases were still present).

The secondary Cl-rich phases were only stable where CSH was present, and we envisage that they progressively breakdown as carbonation reactions consume the CSH around them. The released Cl^- then migrates via diffusion towards the remaining CSH and re-precipitates. This dissolution/precipitation process continues until all of the CSH is reacted (in the case of a limited quantity of cement), at which point the Cl^- would be released back into solution.

The uptake of Cl^- in CO_2-free cement systems concurs with observations undertaken as part of previous experimental buffer/backfill cement studies (Glasser et al., 1998). Cl^- uptake in CO_2-rich systems has also been previously noted as part of borehole stability studies for the deep underground storage of CO_2. Rochelle et al. (2006, 2009) found increased Cl^- uptake in CO_2-rich experiments compared to CO_2-free experiments, and Carey et al. (2007) report a Cl-rich secondary phase in recovered samples of borehole cement that had been exposed to CO_2-rich fluids for 30 years.

The apparent likely occurrence of Cl-rich phases within cementitious repositories, raises the question of whether performance assessment calculations could include them (many current approaches assume conservative, i.e. non-reacting, behaviour of Cl^-). Inclusion of such phases would likely retard the overall predicted migration of ^{36}Cl, lowering eventual releases to the biosphere, and hence improving safety calculations. Equally, they may allow for higher initial loadings of ^{36}Cl in the waste. It would be useful to investigate these Cl-rich phases further.



A) *Backscattered SEM image of main carbonation reaction front.*

B) *Map of Ca abundance (high Ca = pink). Note the high abundance at the carbonation front, and also the limestone grains in cement.*

C) *Map of Cl abundance (High Cl = green). Note its abundance at the edge of Zone 2, just in advance of the main carbonation front.*

Figure 18 High resolution images of a cement carbonation front. Note the abundance of Cl on the partly-carbonated side of the reaction front, and its near absence in the fully-carbonated cement.

7 Concluding remarks

The proceeding sections summarise the findings of our experimental study conducted as part of the FORGE project. This work has allowed identification and quantification of processes occurring during cement carbonation, and this will help inform predictive modelling of repository evolution. The buffer/backfill cement appears to have coped with carbonation well, remaining intact, and with some properties apparently improving (such as reductions in permeability). Uptake of Cl by the cement was also identified, and this could also be beneficial in terms of retarding the mobility of ^{36}Cl. The work also confirmed that cement carbonation leads to a loss of pH buffering to alkaline conditions.

The study highlighted several areas where further investigations could be useful. These include:

- Assessing the likelihood for compositional heterogeneity within the cement as a consequence of settling during and after pouring.
- Quantifying the longevity of the reaction zones identified, and whether they evolve into a single reaction front over long timescales.
- Better defining the likelihood of cement micro-fracturing during carbonation, mechanisms controlling the formation of narrow carbonate precipitation zones, and their impact on permeability.
- Quantifying how efficient secondary phases are at 'armouring' cement from further carbonation, and how the permeability of this carbonated zone changes over time.
- Precise identification of the Cl-rich phases forming within the altered cement, and consideration of the impact such phases could have on ^{36}Cl retardation and repository safety functions.

Carbonation features and secondary phases observed in these experiments using a relatively porous/permeable cement, bear many similarities to those found in far lower porosity/permeability borehole cements used in CO_2-storage operations. There are also similarities to samples of naturally-occurring CSH phases which have been naturally-carbonated over prolonged timescales. A number of common carbonation processes may be operating in all these systems, and consideration of all these sources of information is needed to help provide an overall picture of cement carbonation over a range of temporal and spatial scales.

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